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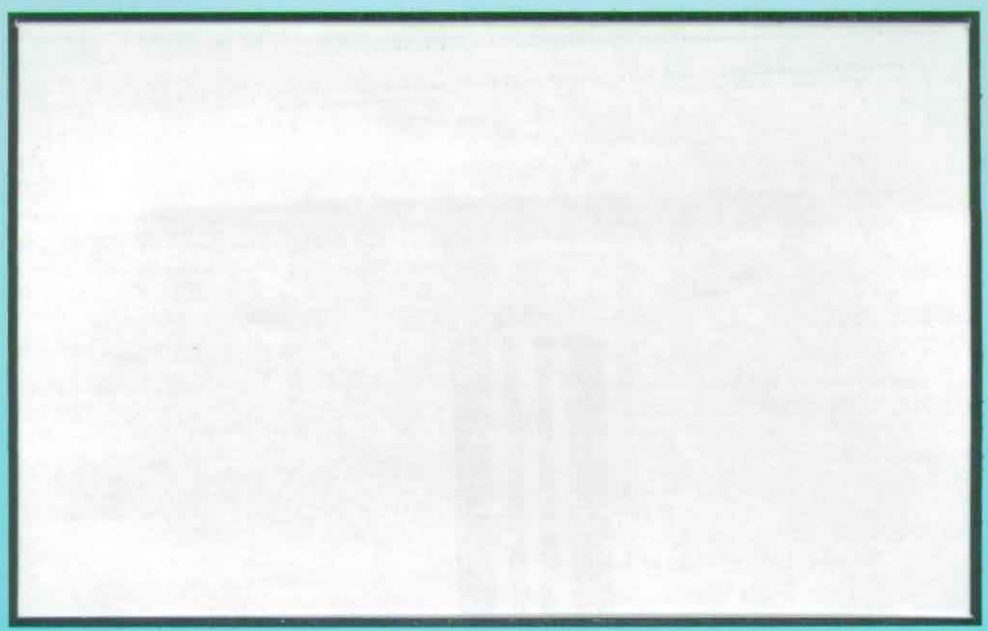

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ANNUAL REPORT

OF THE FIELD-BASED

CLIMATE CHANGE SIMULATION

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EXECUTIVE SUMMARY

1. This report covers the period of the three climate change simulations at the Cerrig–yr–Wyn site at Plynlimon. The experiment has generated a large quantity of hydrochemical data and this report presents an evaluation of this information.

2. The second and third drought simulations had a markedly different effect on trace gas fluxes compared with the first year's experiment. Compared to the control, fluxes of N_2O were reduced by 23% in the second year's simulated drought period compared with 83% in the first year, whereas the third year saw a return to similar levels of emission as the control. Rates of emission of this gas from the wetland as a whole were comparatively small, *c*.0.6 kg N_2O–N ha^{-1} y^{-1}. It seems highly probable that the very low concentrations of NO_3^- and NH_4^+ indigenous in these wetlands severely limits the extent which the process of N_2O production can proceed at this site, irrespective of any prevailing drought conditions.

3. In the first year's treatment, the experimental wetland was transformed from a net sink for CO_2 to a net source. The second and third simulations did not reproduce these findings, with both control and experimental wetlands acting as a net sink for CO_2. However, the experimental wetland accumulated markedly less CO_2 than did the control. It seems likely that an increase in aerobic respiration by soil microorganisms contributed significantly to the flux of CO_2 through the experimental wetland.

4. Methane emissions were significantly reduced by the experimental drought, with the flux of this gas being more than 30% lower from the experimental wetland compared to the control over the 2.5 year period. The most marked effects were observed during the Autumn–Winter months with the flux of CH_4 from the experimental bog being virtually arrested during the re–wetting periods. Redox potential, soil temperature and diffusion rates of CH_4 from the peat to the surface probably control methane emissions from these wetlands. Mean fluxes of CH_4 from the Cerrig–yr–Wyn site (~15–20 mg CH_4 m^{-2} d^{-1}), however, are relatively small compared with previous studies of CH_4 emission rates from temperate peatlands, with a range from 0–700 mg CH_4 m^{-2} d^{-1} being cited.

5. Although there was more rainfall during the second drought simulation, a substantial reduction in water table height was achieved which was of similar magnitude to that observed in the first year. A similar fall in water table height was recorded during the third drought simulation. However, the rate of water table draw-down was much faster in the latter two years than that observed during the first simulation. This probably resulted from a change in the soil physical properties in the upper, fibrous, peat layers, which became hydrophobic in response to drying.

6. Chloride concentrations in interstitial waters in the peat (10cm depth) increased relative to the control during the three drought simulations. On re-wetting, concentrations became similar in both the control and experimental wetland. High evapotranspiration rates in the experimental wetland during drought simulation, coupled with a reversal of hydraulic recharge in the bog, probably caused this effect by enriching the peat-water (10cm depth) with chloride derived from sources lower down the peat profile. Trends in the pH of interstitial waters were closely related to those of sulphate, with more acidic conditions prevailing as sulphate concentrations increased. The most acidic conditions were found in the experimental wetland during the Autumn-Winter periods, which was associated with increased concentrations of sulphate derived from mobilisation of oxidised-S (formed during the drought) from the peat surfaces during re-wetting. This may have important implications for biota in poorly buffered drainage waters, due to the potential for dramatic increases in acidity during large rainfall events, where runoff from the surface peat would be expected to increase.

7. Simulated drought had a dramatic effect on the concentrations of Dissolved Organic Carbon (DOC) and iron in the peat water (10cm depth), with these solutes being significantly reduced relative to the control in each of the three years. These changes are explained by established theories of redox/organic sequestration reactions leading to the co-precipitation of Fe(III) and DOC on the peat surfaces.

1 INTRODUCTION

The following document reports findings from a third year of drought simulation in an experimental wetland at Cerrig-yr-Wyn, plus an overall synthesis of results over the entire 3 year manipulation study. The project follows a previous Welsh Office funded project that has been run jointly by the Institute of Hydrology and the Institute of Terrestrial Ecology between 1988 and 1991.

The main thrust of the study has again been directed at identifying and quantifying the basic mechanisms of hydrochemical interactions within wetlands and the impacts of climate variability- notably a change to generally drier conditions.

1.1 FIELD-SITE INSTRUMENTATION

The natural discontinuities of the Cerrig-yr-Wyn site have made it possible to isolate various sections of the wetland without causing excessive disturbance or interaction with adjacent parts (Figure 1). The uppermost portion of the wetland has been left as a control, it being possible to gain access to the pipe draining the wetland and the catchment area upstream for chemical sampling. Just below the control area, a duralumin barrier has been installed from which an array of 150 mm plastic pipes carry water around the experimental area when the valves are open, or alternatively discharge onto the experimental area when the valves are shut. To prevent erosion and to ensure even wetting, the spillage water is carried to the surface of the wetland in 150 mm pipes, the last of which has been drilled with 25 mm holes along its length. Flows within the gully are measured by a 0.381 m 90° V-notch weir situated below the experimental wetland which has been described in detail by Freeman *et al.*, (1993a). To indicate the efficiency of the by-pass system, flow in the plastic pipes has been measured using "Valeport 3" velocity meters operating in the "pipe full" condition. However, problems with the variable turning threshold of those meters has resulted in their replacement with a second "boxed" V-notch weir.

Streamwater chemistry has been monitored at a number of levels of temporal resolution throughout the experiment. Conductivity, pH, temperature, dissolved oxygen and redox are logged at 15-minute intervals by a pHOX^{R} recorder, with approximately weekly checks on the calibration being made using manual instruments. There were numerous problems with

the pHOX^R meter during 1992/93, particularly regarding the pH electrodes. For this reason, a new scheme of work was adopted in 1993/94 which was based on a more frequent replacement of the pH electrodes. An alternative Hydrolab system has also been deployed in order to assess its comparative reliability, accuracy and ease of operation. Composite water samples continue to be taken using Epic samplers, one sited at the outlet of the control wetland, one in the stream below the experimental wetland when the bypass pipes are not running, and an extra one in the natural pipe between the bypass outfall and the outlet to the experimental wetland when the bypass pipes are running. For the period immediately following the re-wetting of the experimental wetland in Autumn 1992, discrete daily samples consisting of subsamples taken every 30 minutes replaced the weekly composites. This enabled the daily variability of solute concentrations to be assessed and this new system has been used extensively in the 1993/94 drought simulation.

Peat-water samples were extracted, at two weekly intervals, from the top 10 cm of the peat profile using samplers placed at 2.5 m intervals along a transect down the two wetland areas. Five samplers were installed in each of the two wetlands. The soil solution samplers were constructed as described by Freeman *et al.,* (1993a), using a design aimed at minimizing the extraction volume and any unnecessary dead volumes. This ensured that excessive disturbance of the wetland was avoided and that the integrity of the extracted sample (in particular the redox potential) was not affected. The ends of ten 2.5 cm^3 Plastipak^R syringes were cut-off at 1-1.5 cm from the luer tip. The luer end was retained and packed with glass wool, and connected to Tygon^R Autoanalyser transmission tubing to the surface, where suction could be applied using a 30 cm^3 Plastipak^R syringe.

Dissolved oxygen, pH and temperature were measured in the field using standard electrometric techniques. Water table levels were measured using a 5 cm radius unlined dip well (Ingram, 1983) sited in the centre of the transect through each wetland.

Measurements of CO_2, CH_4 and N_2O fluxes from the wetlands were made, at two weekly intervals, using a closed chamber technique. Five 4.5l capacity translucent, polyethylene, wide neck bottles, which were sawn-off at the base, were installed along a transect (2.5 m spacing) in each wetland. A small hole was drilled in the lid of each bottle, and a short piece

of Tygon^{R} Autoanalyser transmission tubing was inserted into the holes to give an airtight fit. Gas samples were collected during daytime, after a two hour incubation period, using 10 cm capacity glass Pressure-Lok^{R} Gas sample syringes. Each chamber was left open in-between sampling dates to ensure that growth of wetland vegetation within the chambers was unimpeded.

1.2 CHEMICAL ANALYSIS OF PEAT-WATER AND DRAINAGE WATERS

Samples of peat-water and drainage waters were sampled at regular intervals, as described above. On return to the laboratory, the samples were filtered through Whatman 0.45 μm diameter cellulose nitrate filters, and samples analysed for Na, K, Ca, Mg, Fe, NH_4, NO_3-N, PO_4-P, SO_4, Cl, Si, Dissolved Organic Carbon (DOC) and, for drainage water only, Alkalinity. Na, K, Ca and Mg were measured by Ion Chromatography (until 08/94), using a Dionex 2000i/sp system comprising a CS12 analytical column and conductivity detection with Auto Self-Regenerating Suppression, and thereafter by flame atomic emission spectrophotometry (Na, K), or flame atomic absorption spectrophotometry (Ca, Mg, Fe), respectively. Chloride, NO_3-N, PO_4-P and SO_4 were measured by Ion Chromatography, using an AS4A analytical column and conductivity detection with Auto Self-Regenerating Suppression. Ammonium was measured by segmented-flow colorimetry (Indol-phenol blue) using a Skalar Autoanalyser (until 03/94), and thereafter by Ion chromatography (CS12 analytical column). Silicon was measured by Autoanalyser using a standard molybdate-blue method. Dissolved Organic Carbon was determined by Autoanalyser following a UV-digestion technique, and colorimetric detection. Alkalinity was determined by Gran-titration.

1.3 CHEMICAL ANALYSES OF GAS SAMPLES

Gases were analysed by Gas Chromatography using an AI Cambridge model 92 Gas Chromatograph (GC). The GC was fitted with two Porapak QS analytical columns, one of which was connected to a flame ionisation detector with a $CO_2 \rightarrow CH_4$ catalytic convertor (to detect carbon dioxide as well as methane), and the other to an electron capture detector operating at 350°C (to detect N_2O). Separations were carried out at 35°C with N_2 carrier gas at 30 cm^3 min^{-1}.

2 RESULTS OF THE SECOND AND THIRD CLIMATE CHANGE SIMULATIONS

The following section relates details of the data generated in the second and third simulated drought experiments to that generated in the first year of study. The final stage of the third manipulation study has only just been completed. We are at an advanced stage in the chemical analysis, although full results for some determinants are not yet available. Data is presented up until November 1994 or January 1995 for peat–water chemistry and trace gas fluxes, respectively.

2.1 CHANGES IN TRACE GAS EMISSION

The second and third simulated climatic change experiments affected trace gas emissions somewhat differently from the first simulation. Trace gas emissions in the second year were probably influenced by the far wetter conditions of 1993/94.

2.1.1 **nitrous oxide emissions**

The impacts on nitrous oxide in year one were among the most pronounced of all effects observed, with the flux of this gas being all but arrested by the drought simulation (Figure 2). At the time we suggested that this could have been brought about by elimination of the flow of nitrate (the substrate for denitrification/N_2O production) through the experimental wetland. However, the effects of the second and third drought simulations were far less dramatic, with only a 23% reduction in emissions being detected in the second year (as opposed to 83% in the first year), and a return to similar levels of emission as the control in the third year (Figures 3 and 4).

Mechanisms controlling the rate of release of N_2O from wetlands are known to be fairly complex. Nitrous oxide is produced during the processes of both denitrification and nitrification; it is an intermediate in the former and a by–product of the latter. Bandibas *et al.*, (1994) cited the following conditions to be favourable to N_2O production: i) medium–high soil water content, limiting the O_2 diffusion rate; ii) high mineral–N (NO_3^- or NH_4^+) availability and iii) high organic–C availability. The positive effect of partially anoxic conditions on N_2O production during denitrification has been demonstrated by Hochstein *et al.*, (1984), who found that pure cultures of *Paracoccus halodenitrificans* reduced NO_3^- to N_2

in the absence of O_2, under partially anoxic conditions production of N_2O was favoured, whereas in aerobic conditions NO_2^- was formed. Under field conditions, Bandibas *et al.*, (1994) reported that the highest rates of N_2O production in the soil occurred under saturated (but not waterlogged) conditions. Moreover, it has been found that the rate of oxygen consumption by soil microorganisms is more important than the rate of its dissolution, which may explain the apparent observation of aerobic denitrification (Russell, 1977). Bandibas *et al.*, (1994) also reported that N_2O emissions in 18 soils they tested were not primarily determined by the process rate (ie nitrification/denitrification), but by the relative N_2O production, which can be defined as the percentage of reduced or oxidised substrate forming N_2O (ie denitrification: $N_2O*100/[N_2O+N_2]$;
nitrification: $N_2O*100/[N_2O+NO_2^*]$).

Any one or a combination of these factors may be affecting N_2O production at this site. It could be postulated that the slower rate of water table drawdown in the experimental bog during the first year may have had an adverse effect on N_2O production (*via* relative O_2 saturation) compared to the more rapid water table falls in the second and third years. However, at which level of control this may have exerted an influence, at the substrate level (N-mineralisation/nitrification) or the process/relative N_2O production levels (nitrification/denitrification), is not easy to quantify under field conditions. The observations of a general reduction in N_2O production in the experimental wetland during simulated drought conditions is contrary to results reported by Freeman *et al.*,(1993b) who, in laboratory manipulations of peat-cores subjected to simulated drought conditions, reported a significant increase in N_2O production to values exceeding 1 mg N_2O m^{-2} d^{-1}. Freeman and co-workers attributed this to an increase in mineralisation (and nitrification) in the peat providing substrates for nitrification and denitrification and, therefore, increased N_2O production.

The mean nitrous oxide flux from the control wetland over the three simulated drought periods was 0.29 mg N_2O m^{-2} d^{-1}, which compares with a value of 0.11 mg N_2O m^{-2} d^{-1} reported by Freeman *et al.*, (1993b) in laboratory investigations of peat-cores sampled from Cerrig-yr-Wyn, and with values of <0.72 and 0.023 mg N_2O m^{-2} d^{-1} respectively, observed by Hemond (1983) and Urban *et al.*, (1988). Taken over the complete 2.5 year period (Figure 5), rates of N_2O emission from the Cerrig-yr-Wyn site were ~0.62 kg N_2O-N ha^{-1} y^{-1}, which

compares with values of 0.19–0.80 for deciduous forests USA, and 0.99–2.1 kg N ha^{-1} y^{-1} for coniferous forests USA (Goodroad and Keeney, 1984), respectively, and with rates of 1.1–2.7 kg N ha^{-1} y^{-1} for Amazonian tropical rainforests (Keller *et al.*, 1986).

Nitrification of mineralised ammonia is an important source of nitrate for denitrification in wetlands (Seitzinger, 1994). This has been demonstrated by several studies from measurements of ^{15}N $-N_2$ production from peat-cores following ^{15}N–NH_4^+ additions (Patrick and Reddy, 1976; DeBusk and Reddy, 1987; Reddy *et al.*, 1989). It seems highly likely that the low nitrate concentrations indigenous in the wetlands at Cerrig-yr-Wyn, which probably result from a combination of low N-mineralisation rate and competition for the substrate for nitrification (ie NH_4^+) by plants, severely limits the extent at which the process of N_2O production can proceed at this site, irrespective of any prevailing drought conditions.

2.1.2 CO_2 emissions

During the first year's drought simulation period, the control wetland acted as a sink for carbon dioxide (daytime), while the wetland undergoing simulated drought was transformed from a net sink to a net source of this gas (Figure 6; weeks 0–20). The following two years did not reproduce these findings , although there was a similarity in the trends. Both control and experimental wetlands were sinks for CO_2 (Figure 6; weeks 54–72,103–117). However, the drier experimental wetland accumulated substantially less carbon dioxide than the control. These observations suggest that either the rate of photosynthesis by the vegetation in the experimental wetland undergoing simulated drought was reduced as a result of stress, and/or else that the rate of production of CO_2 in the soil (from aerobic respiration) had increased in response to drying (see also section 2.2). These observations are in accordance with those of Moore and Knowles (1989), who also reported that simulated drought significantly increased the flux of CO_2 through wetlands.

2.1.3 methane emissions

In the first simulation, we noted that in contrast to CO_2, both control and experimental wetlands acted as sources of methane (Figure 7; weeks 0–20). The rate of release from the control appeared relatively constant. However, the release from the experimental wetland appeared distinctly bi-phasic, with an initial phase in which the rate of release was greater than that of the control, but which was followed by a second phase (~week 7 onwards), with a markedly lower rate of release. The trend for lower methane release from the experimental wetland was maintained during the second and third years (Figure 7). The difference between the two wetlands was almost as great as that seen for N_2O in the first year of the study with the overall release of methane over the 2.5 year period being 30% lower than that of the control.

Figure 7 also shows that the most marked effects on CH_4 emissions occurred during the Autumn–Winter (re-wetting) periods. The emissions of CH_4 from the experimental bog were virtually arrested during these periods (weeks 22–45; 75–100), whereas, in contrast, the emissions of CH_4 from the two wetlands during the actual simulated drought periods were more similar. This suggests that relative diffusion rates of CH_4 through the peat may be important in contributing to these observations. Diffusion of CH_4 from the peat to the surface would be expected to be lower through the waterlogged control wetland compared with the drought impacted experimental wetland during the Summer months, and this may offset an intrinsically greater process rate in the former. During the re-wetting periods, however, relative diffusion rates in the two wetlands may be expected to more similar, and the observed differences would be more likely to reflect differences in the process rate in these two wetlands. The rate of emission of methane from these wetlands is clearly seasonal (peak rates in the Summer), which supports the view that methane emissions from wetlands are controlled by soil temperature (see Figure 18; peat (10cm depth) temperature), acting on microbial metabolism, as well as diffusion (Crill *et al.*, 1988; Lansdown *et al.*, 1992).

The differences in the process rate in the two wetlands are explained by changes from anaerobic (control) to more aerobic (experimental) conditions impacting upon methanogenic microorganism populations in these wetlands. The fact that the process rates are different in the two wetlands during the re-wetting periods suggests that these populations have not

recovered in the experimental wetland between the three simulated drought periods. However, it is also possible that high concentrations of sulphate in the peat interstitial waters in the experimental bog during the re-wetting periods (see section 2.2; Figure 11) may have had an adverse effect on CH_4 production. In surface soils, the presence of terminal electron acceptors, such as SO_4, may result in methanogens being outcompeted by other anaerobic microorganisms (Oremland, 1988).

The mean fluxes of CH_4 from the control and experimental wetlands over the 2.5 year period were 21 and 14.5 mg CH_4 m^{-2} d^{-1}, respectively. This compares with rates of 0.6–68.4 mg CH_4 m^{-2} d^{-1} reported for Michigan peatlands with plant communities dominated by *Chamaedaphne calyculata*, an ericaceous shrub, and 11.5–209 mg CH_4 m^{-2} d^{-1} in peatland areas dominated by plants with aerenchymatous tissues, such as *Carex oligosperma*. The latter are believed to play a significant role in altering the methane flux from peatland ecosystems by directly transporting methane from anaerobic peat to the surface (Shannon and White, 1994).

Moore and Knowles (1990) cited a range of 0–700 mg CH_4 m^{-2} d^{-1} from a review of a number of studies of methane emission rates from peatlands in temperate to subarctic locations, often with a strong component of seasonal and spatial variability. Values for Cerrig-yr-Wyn , therefore, are in the lower end of this quoted range of CH_4 emission rates. It is also interesting to note that the values obtained for Cerrig-yr-Wyn under field conditions differ markedly from those observed for peat-cores from the same site, manipulated under laboratory conditions.

Freeman and co-workers (1993b) reported a mean flux of 230 mg CH_4 m^{-2} d^{-1} from control cores at 11°C. These cores, however, were maintained under saturated but <u>not</u> waterlogged conditions; the latter is often found under field conditions (see Figure 8 - water table height). It is possible that the rate of diffusion of CH_4 from the peat to the headspace in the peat-cores in the laboratory was far greater than was possible under field conditions, which may partly explain the far greater rates of emission of this gas under laboratory conditions.

2.2 HYDROCHEMICAL RESPONSES WITHIN THE PEAT

In Figure 8, it can be seen that despite the greater rainfall during the second drought simulation a substantial reduction in water table height was induced (weeks 54–72). The rapidity with which the water table fell following diversion of the inflow water was far greater than we anticipated based upon the findings of the previous year's simulation. This scenario was repeated during the third drought simulation (weeks 103–117). This suggests that the first year's drought simulation (weeks 0–20) had brought about a change in the peat structure which had not returned to its original state despite a prolonged period of re-wetting. The most likely explanation is that the period of drought simulation in year 1 caused the upper layers of fibrous peat to become hydrophobic. Field observations at Plynlimon following the 1976 drought showed that major structural changes occurred in deep peats at the head of the Wye catchment. These persisted for many years following re-wetting.

As in our laboratory experiments, we also found a marked increase in peatwater (10cm depth) chloride concentrations in the experimental wetland, compared to the control, during the simulated drought periods (Figure 9;weeks 0–20;54–72;103–117). These changes can be explained by a concentration effect caused by relatively high rates of evapotranspiration in the experimental bog during the summer months effecting (via capillary forces at the peat surface) a reversal in the direction of hydraulic recharge in the bog from vertically downwards, during high water table (winter) conditions, to vertically upwards, during low water table (simulated drought) conditions. Such a reversal of direction of hydraulic recharge has been reported, under similar conditions, in studies of the hydrological management of cutover peatlands (Heathwaite, 1994).

In earlier laboratory investigations of peat-cores from the Cerrig-yr-Wyn site, we found that peatwater chloride concentrations increased progressively with depth down the peat profile (Freeman *et al.*, 1993c). It would be expected, therefore, that if the direction of hydraulic recharge in the experimental bog was reversed during drought simulation, the peatwater (10cm depth) would be enriched in chloride derived from pore-water sources deeper in the peat profile. It is also interesting to note that although, during each re-wetting period, there is a similarity in the concentrations in both the control and experimental wetlands, temporal changes in chloride concentrations in the experimental wetland seem to have lagged those

of the control during the first year. During weeks 28–50, the chloride concentration appears to have increased, and peaked, at a much slower rate in the experimental wetland. It seems that chloride moved down the valley as a pulse and it took *c.* 5 weeks longer for the pulse to reach the lower experimental wetland. Interestingly, the pulse was not detectable at all during the second year. However, this may have been due to the far greater rainfall, and hence greater rate of flow of water through the wetlands.

At the start of the first year of drought simulation, peatwater (10cm depth) pH was higher in the experimental wetland than in the control, but then changed, on week seven, with the pH becoming lower than that of the control. The pH was lower in the control wetland, only occasionally from then onwards (Figure 10). However, the second year of drought simulation resulted in a marked, complete separation of the two wetlands with the control remaining less acidic throughout the remainder of our measurements. This scenario has been repeated during the third year of drought simulation, to date.

The change to more acidic conditions in the experimental wetland is associated with changes in sulphate abundance. From week seven onwards, sulphate concentrations too have generally remained greater in the experimental wetland than in the control (Figure 11). Moreover, it can be seen that plots of SO_4^{2-} concentrations in the two wetlands are broadly the inverse of those of pH over the three years, with periods of high concentrations of sulphate in the wetlands being associated with lower pH measurements in the peatwater (Figures 10 and 11). It is also interesting to note that the most acidic conditions in the experimental wetland occur during the re-wetting periods. This, most likely, results from mobilisation of sulphate from the peat surfaces during re-wetting. The sulphate is probably derived from oxidation of reduced organic and inorganic sulphur (sulphides) in the experimental bog during low-water table (aerobic, higher redox potential) conditions (Ponnamperuma, 1972). The fact that the abundant sulphate can be readily mobilized may have important implications for the biota in poorly buffered drainage waters, due to dramatic increases in acidity during large rainfall events, as reported by Gosling and Baker (1980).

Other factors which may lead to periodic acid episodes include the occurrences of large, marine-derived, salt events. Large concentrations of neutral salts impacting upon the

wetlands, from occult, dry and wet deposition sources, can lead to short-term changes in peatwater chemistry (Chapman, 1994). The main effects are a lowering of pH and a change in the Na:Cl molar ratio (lower) in the peatwater as a result of ion exchange of Na^+ for H^+ on the exchange sites on the peat surface. One such event was observed during the second year's re-wetting period (week 82). It can be seen in Figures 9 and 10 that a large peak in chloride concentrations in the wetlands (Cl^- values >9 mg/l) was accompanied by a sharp fall in pH in the two bogs. An examination of Figures 9 and 12 also reveals a fall in the Na:Cl molar ratio, from a value of 1.15 immediately preceding the salt event, to a value of 0.68 during the event itself.

It can be seen in Figures 13 and 14 that drought simulation in the experimental wetland had a dramatic effect on Dissolved Organic Carbon (DOC) and Fe concentrations, with these solutes being significantly reduced relative to the control in each of the three years. These changes can be explained by established theories of redox/organic sequestration processes leading to the co-precipitation of Fe(III) and DOC on the peat surfaces. Moreover, the more humic-rich fractions of DOC tend to adsorb readily on these precipitates, thus enhancing the whole process (Tipping and Woof, 1990; Freeman *et al.*, 1993c).

Precipitation of large molecular mass humic acids is also likely to be promoted by the increase in acidity in the experimental wetland induced by drought simulation. Microbial processes are also likely to contribute to the fall in DOC concentrations in the experimental bog. In the more anaerobic (low redox potential) conditions normally found in wetlands, a greater proportion of end products of metabolism include low molecular weight organic solutes, such as aldehydes and ketones (Ponnanperuma, 1972; Freeman *et al.*, 1993c), whereas in more aerobic (low-water table) conditions, microbial metabolism is more likely to favour oxidative , inorganic carbon (CO_2) end products. This also partly explains the differences in net fluxes of CO_2 from the two bogs, since higher rates of CO_2 production from mineralisation by soil microbes in the experimental wetland may be expected to make a significant contribution to the net flux of CO_2 through the bog. The very seasonal patterns of DOC and Fe concentrations in the wetlands (peak concentrations in the summer) strongly supports the view that Fe exists in soil solution predominantly as organic complexes, and that these solutes are under strong biological control (Hughes *et al.*, 1990; Emmett *et al.*, 1994).

Concentrations of major inorganic plant nutrients (N, P, K) in the two wetlands were generally very low (Figures 15–17). Indeed, concentrations of PO_4–P were generally below analytical detection limits. No significant differences in NH_4^+ concentrations were observed in any of the three years, whilst concentrations of NO_3^- and K^+ tended to be smaller in the experimental wetland. This scenario, of reduced NO_3^- concentrations following drought simulation, is contrary to earlier laboratory studies of experimental peat–cores, which revealed a significant increase in nitrate concentrations relative to the control. Freeman an co–workers (1993c) attributed the increase in NO_3^- concentrations (10cm depth) in the experimental peat–cores to an increase in the population of ammonium oxidising bacteria. The fact that this scenario was not repeated under field conditions suggests that other factors, possibly competition for the substrate (NH_4^+) by plants, were limiting the populations of these microorganisms at this site. It is interesting to note, however, that in both year 1 and 2, nitrate concentrations in the wetlands peaked in late winter–early spring, which may suggest that ammonium oxidising /nitrifying microorganism populations were active in the wetlands before the onset of the new season of plant growth.

3 WORK IN-PROGRESS

The next stage of the Phase two study has now been initiated; namely, an experiment to assess the effects of an increase in precipitation on the wetlands in terms of gaseous emission rates (N_2O, CO_2, CH_4) and hydrochemical changes within the wetlands. At the present time, two new wetlands at Cerrig-yr-Wyn, one of which is a new control area, are being monitored for a period prior to the commencement of increased hydrological loading to the new experimental wetland area.

4 LIST OF PUBLICATIONS ARISING FROM THE PROJECT

Freeman, C., Emmett, B.A. and Reynolds, B., 1991. Wetland biogeochemistry and the consequences of global warming. *ITE Annual Report* 1990/91, HMSO, p 28–30.

Gammelguaard, A., Freeman, C., and Lock, M.A., 1992. The measurement of electron transport system activity in Sphagnum-derived peat. *Soil Biology and Biochemistry* 25: 505–507.

Freeman. C., Hawkins, J., Lock, M.A and Reynolds, B., 1993. A laboratory perfusion system for the study of biogeochemical responses of wetlands to climatic change. In: Gopal B., Hillbricht-Ilkowska, A. and Wetzel, R.G. (eds). *Wetlands and Ecotones: Studies on Land-Water Interactions*, p 75–84.

Freeman, C., Lock, M.A., and Reynolds,B., 1993. Impacts of climatic change on peatland hydrochemistry; a laboratory based experiment. *Chemistry and Ecology*, 8: 49–59.

Freeman, C., Lock, M.A. and Reynolds, B., 1993. Fluxes of carbon dioxide, methane and nitrous oxide from a Welsh peatland following simulation of water table draw-down: Potential feedback to climatic change. *Biogeochemistry*, 19: 51–60.

Freeman, C., Lock, M.A. and Reynolds, B., 1993. Climatic change and the release of immobilised nutrients from Welsh riparian wetland soils. *Ecological Engineering*, 2: 367–373.

Freeman, C., Hudson, J., Lock, M.A. and Reynolds, B., 1993. A field-based approach to investigating potential impacts of drought induced by climatic change upon wetlands. In: Kundzewicz, Z.W., Rosbjerg, D., Simonivic, S.P and Takeuchi, K. (eds), *Extreme Hydrological Events: Precipitation, Floods and Droughts*, pp 151–155, IAHS Press, Wallingford, UK.

Pind, A.., Freeman, C. and Lock, M.A., 1994. Enzymic degradation of phenolic materials in peatlands- measurement of phenol oxidase activity. *Plant and Soil*, 159: 227–231.

Freeman, C., Gresswell, R., Guasch, H., Hudson, J., Lock, M.A., Reynolds,B., Sabater, F. and Sabater, S. 1994. The role of drought in the impacts of climatic change on the microbiota of peatland streams. *Freshwater Biol.*, 32: 223–230.

5 REFERENCES

Bandibas, J., Vermoesen, A., De Groot, C.J. and Van Cleemput, O., 1994. The effect of different moisture regimes and soil characteristics on nitrous oxide emission and consumption by different soils. *Soil Science*, 158, 106–114.

Chapman, P.J., 1994. Hydrogeochemical processes influencing episodic streamwater chemistry in a small headwater catchment, Plynlimon, Mid-Wales. PhD thesis. Imperial College, London.

Crill, P.M., Barlett, K.B., Harriss, R.C., Gorham, E., Verry, E.S., Sebacher, D.L., Madsar, L. and Sanner, W. 1988. Methane flux from Minnesota peatlands. *Global Biogeochem. Cycles* 2(4): 371–384.

DeBusk, W.F. and Reddy, K.R., 1987. Removal of floodwater nitrogen in a cypress swamp receiving primary wastewater effluent. *Hydrobiologia*, 153: 79–86.

Emmett, B.A., Hudson, J.A., Coward, P.A. and Reynolds, B., 1994. The impact of a riparian wetland on streamwater quality in a recently afforested upland catchment. *J. Hydrol.*, 162: 337–353.

Freeman, C., Hudson, J., Lock, M.A. and Reynolds, B., 1993a. A field-based approach to investigating potential impacts of drought induced by climatic change upon wetlands. In: Kundzewicz, Z.W., Rosbjerg, D., Simonivic, S.P and Takeuchi, K. (eds), *Extreme Hydrological Events: Precipitation, Floods and Droughts*, pp 151–155, IAHS Press, Wallingford, UK.

Freeman, C., Lock, M.A. and Reynolds, B., 1993b. Fluxes of carbon dioxide, methane and nitrous oxide from a Welsh peatland following simulation of water table draw-down: Potential feedback to climatic change. *Biogeochemistry*, 19: 51-60.

Freeman, C., Lock, M.A., and Reynolds,B., 1993c. Impacts of climatic change on peatland hydrochemistry; a laboratory based experiment. *Chemistry and Ecology*, 8: 49-59.

Goodroad, L.L and Keeney, D.R. 1984. Nitrous oxide emissions from forest, marsh, and prairie ecosystems. *J.Environ. Qual.* 13, 448-452.

Gosling, L.M. and Baker, S.J., 1980. Acidity fluctuations at a Broadland site in Norfolk. *J. Appl. Ecol*, 17: 479-490.

Heathwaite, A.L., 1994. Hydrological management of a cutover peatland. *Hydrological Processes*, 8: 245-262.

Hemond, H., 1983. The nitrogen budget of Thoreaus bog. *Ecology*, 64: 99-109.

Hochstein, L.I., Betlach, M. and Kritikos, G., 1984. The effect of oxygen on denitrification during steady-state growth of *Paraccocus halodenitrificans*. *Arch. Microbiol.* 137: 74-78.

Hughes, S., Reynolds, B. and Roberts, J.D., 1990. The influence of land management on the concentrations of dissolved organic carbon and its effects on the mobilization of aluminium and iron in podzol soils in Mid-Wales. *Soil Use and Management*, 6: 137-145.

Ingram, H.A.P., 1983. Hydrology, In: *Ecosystems of the World 4a; Mires; Swamp, Bog, Fen, and Moor*, ed. Goodall, D.W., Elsevier, Amsterdam, 67-158.

Keller, M., Kaplan, W.A and Wofsy, S.C. 1986. Emissions of N_2O, CH_4 and CO_2 from tropical forest soils. *J. Geophys. Res.* 91, 791-802.

Lansdown, J.M., Quay, P.D. and King, S.L. 1992. CH_4 production via CO_2 reduction in a temperate bog: A source of ^{13}C-depleted CH_4. *Geochim. Cosmochim. Acta*. 56, 3493-3503.

Moore, T.R. and Knowles, R., 1989. The influence of watertable levels on methane and carbon dioxide emissions from peatland soils. *Can. J. Soil Sci.* 69: 33-38.

Moore,T.R and Knowles, R., 1990. Methane emissions from fen, bog and swamp peatlands in Quebec. *Biogeochemistry*, 11, 45-61.

Oremland, R.S. 1988. Biogeochemistry of methanogenic bacteria. p642-705. In: A.B.J Zehnder (ed.) Biology of anaerobic microorganisms. John Wiley & Sons, New York.

Patrick, W.H. and Reddy, K.R., 1976. Denitrification reactions in flooded soils and water bottoms.: dependance on oxygen supply and ammonium diffusion. *J. Environ. Qual.* 4: 469-471.

Ponnamperuma, F.M., 1972. The chemistry of submerged soils. *Advances in Agronomy*, 24, 29-96.

Reddy, K.R., Patrick, W.H. Jr. and Lindau, C.W.,1989. Nitrification-denitrification at the plant root-sediment interface in wetlands. *Limnol. Oceanogr*. 34; 1004-1013.

Russell, R.S., 1977. *Plant root systems: Their function and interaction with the soil.* McGraw-Hill , London, p 277.

Seitzinger, S.P., 1994. Linkages between organic matter mineralization and denitrification in eight riparian wetlands. *Biogeochemistry,* 25: 19-39.

Shannon, R.D. and White, J.R., 1994. A three-year study of controls on methane emissions from two Michigan peatlands. *Biogeochemistry*, 27, 35-60.

Tipping, E. and Woof, C., 1990. Humic substances in acid organic soils: Modelling their release to the soil solution in terms of humic charge. *J. Soil Sci.* 41: 573–586.

Urban, N.R., Eisenreich, S.J. and Bayley, S.E., 1988. The relative importance of denitrification and nitrate assimilation in mid–continental bogs. *Limnol. Oceanogr.* 33: 1611–1617.

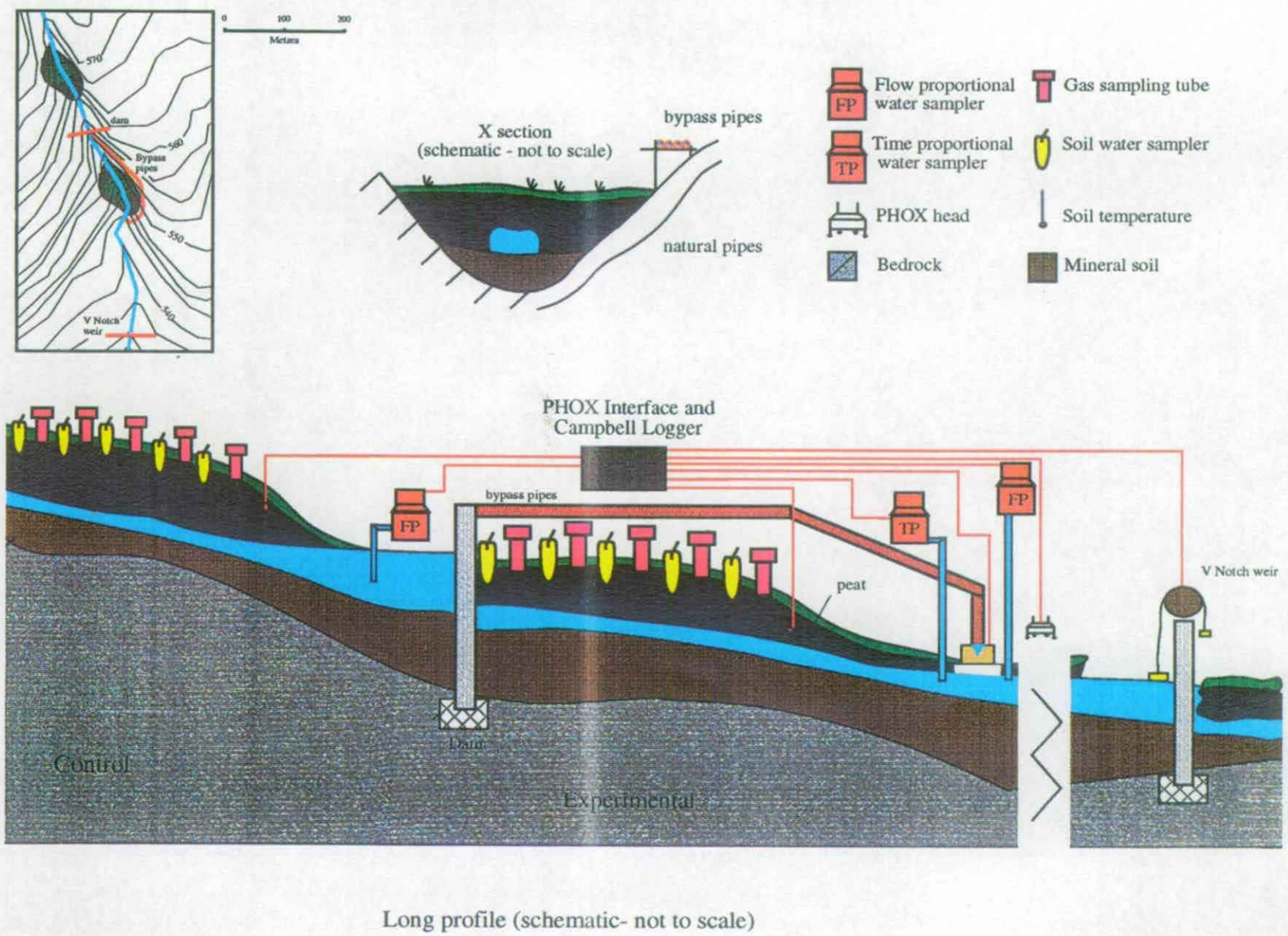

Figure 1. Schematic diagram of the experimental site.

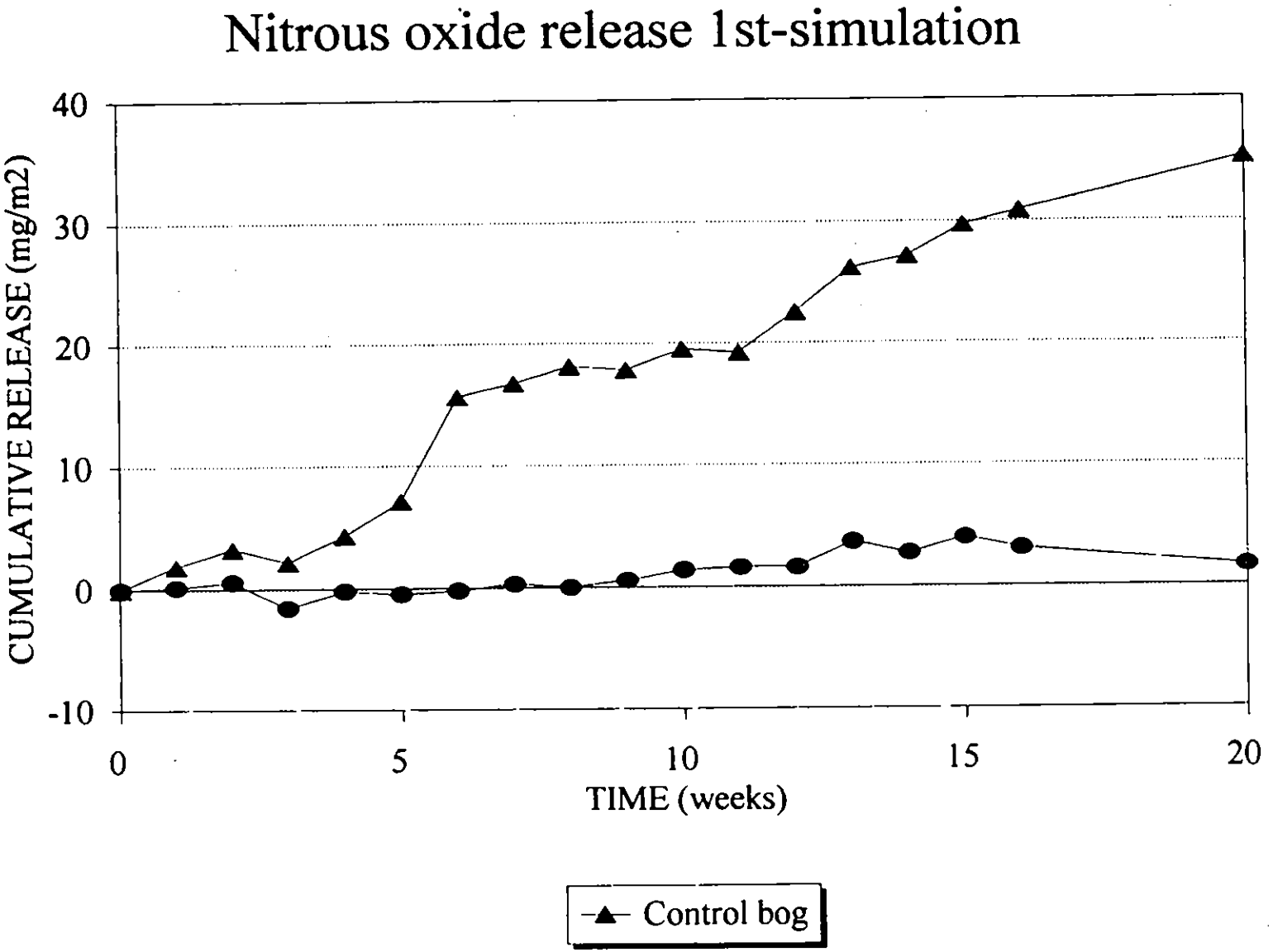
Nitrous oxide release 1st-simulation
CUMULATIVE RELEASE (mg/m2)
40
30
20
10
0
-10
0
5
10
15
20
TIME (weeks)
Control bog

Figure 2

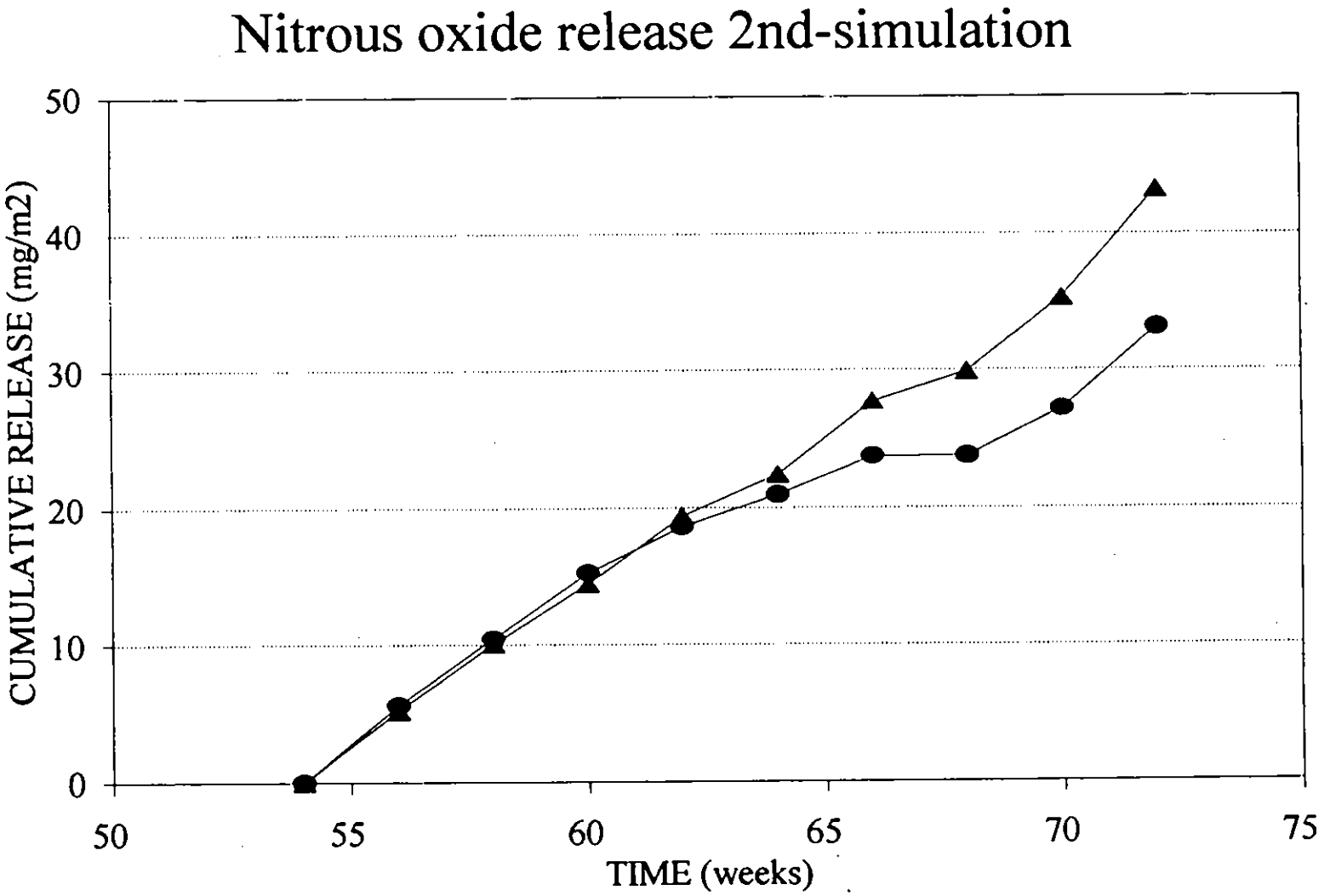
Nitrous oxide release 2nd-simulation
CUMULATIVE RELEASE (mg/m2)
0
10
20
30
40
50
50
55
60
65
70
75
TIME (weeks)

Figure 3

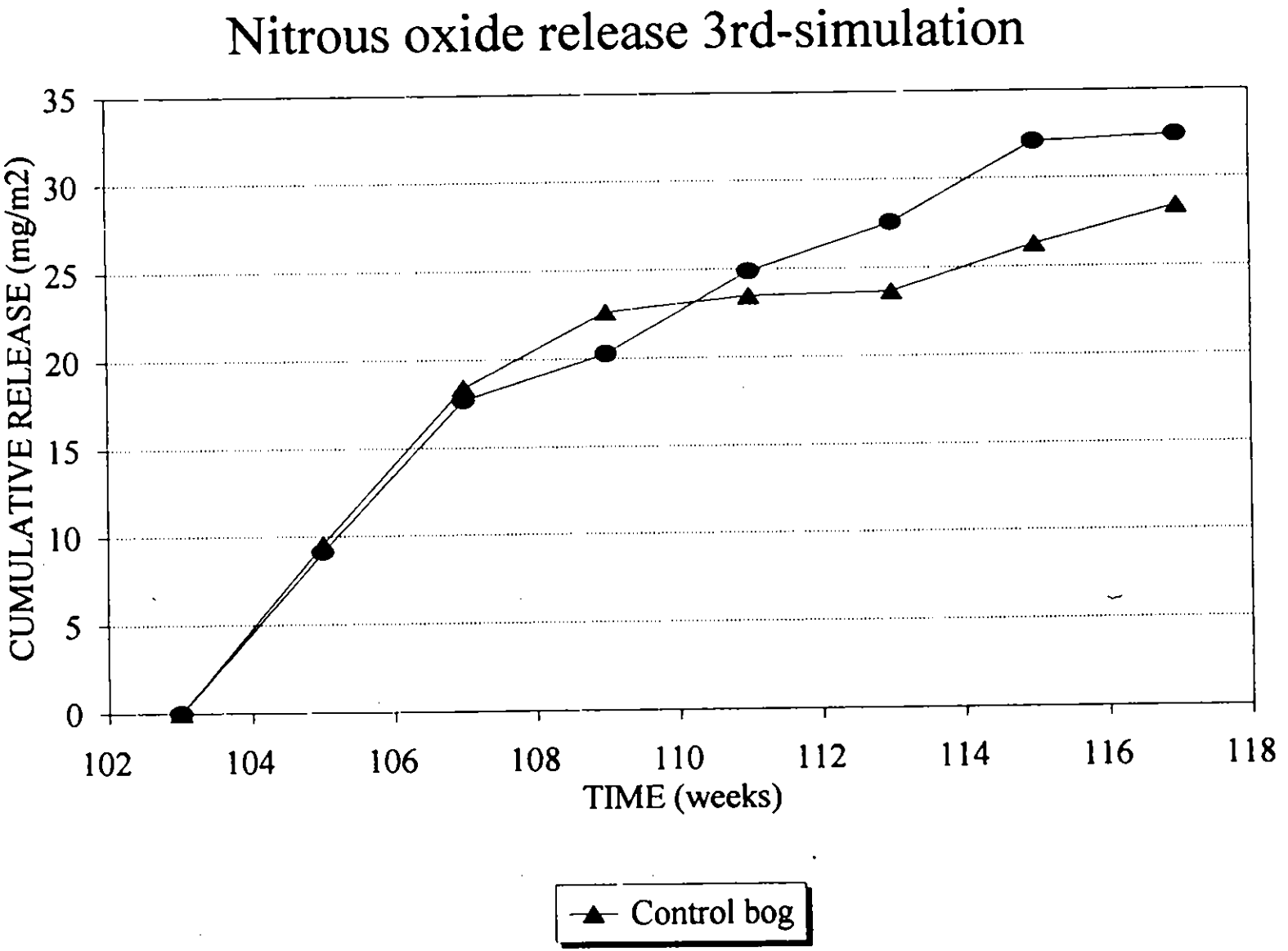
Nitrous oxide release 3rd-simulation
CUMULATIVE RELEASE (mg/m2)
0
5
10
15
20
25
30
35
102
104
106
108
110
112
114
116
118
TIME (weeks)
Control bog

Figure 4

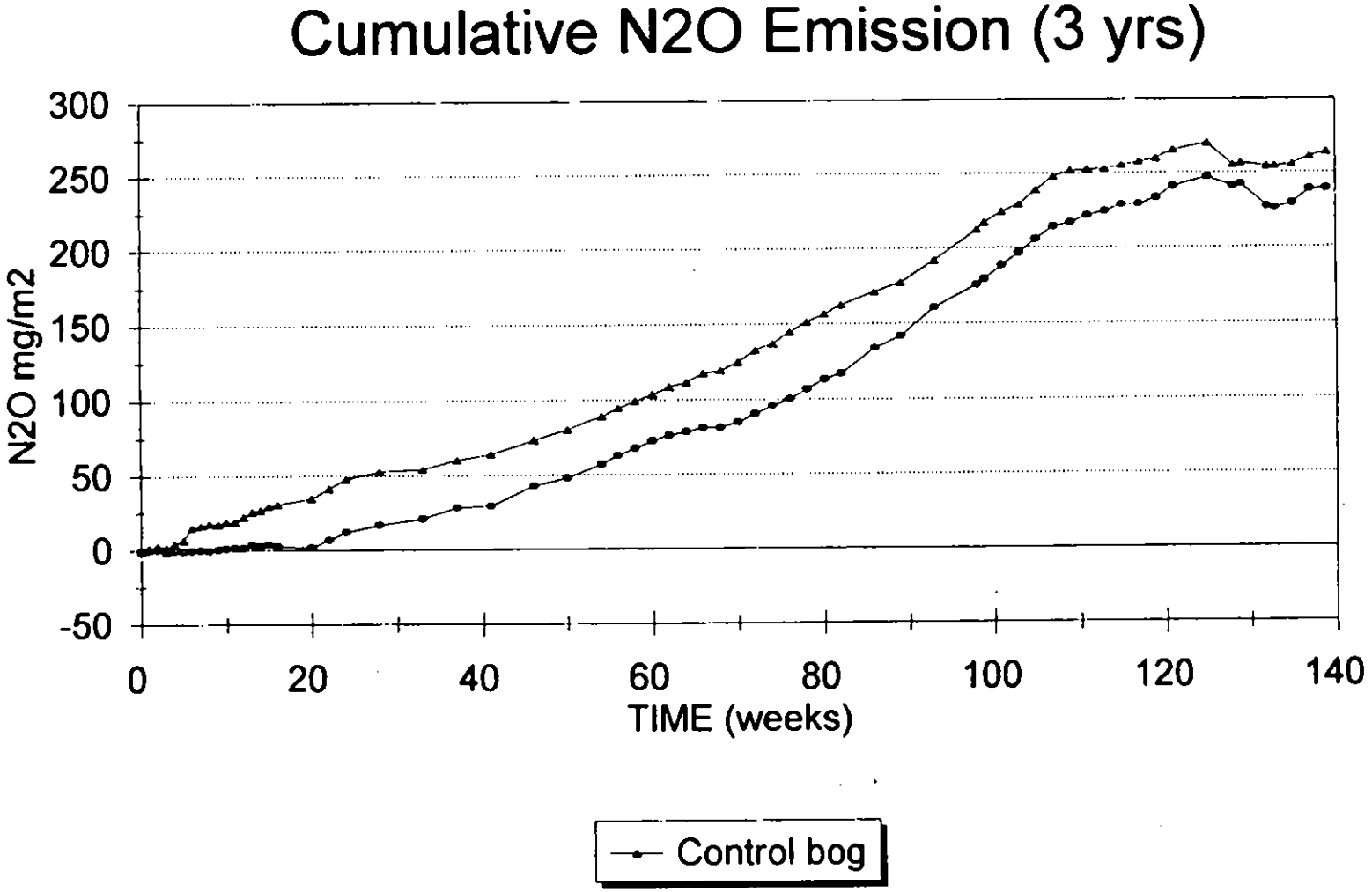
Cumulative N2O Emission (3 yrs)
N2O mg/m2
300
250
200
150
100
50
0
-50
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 5

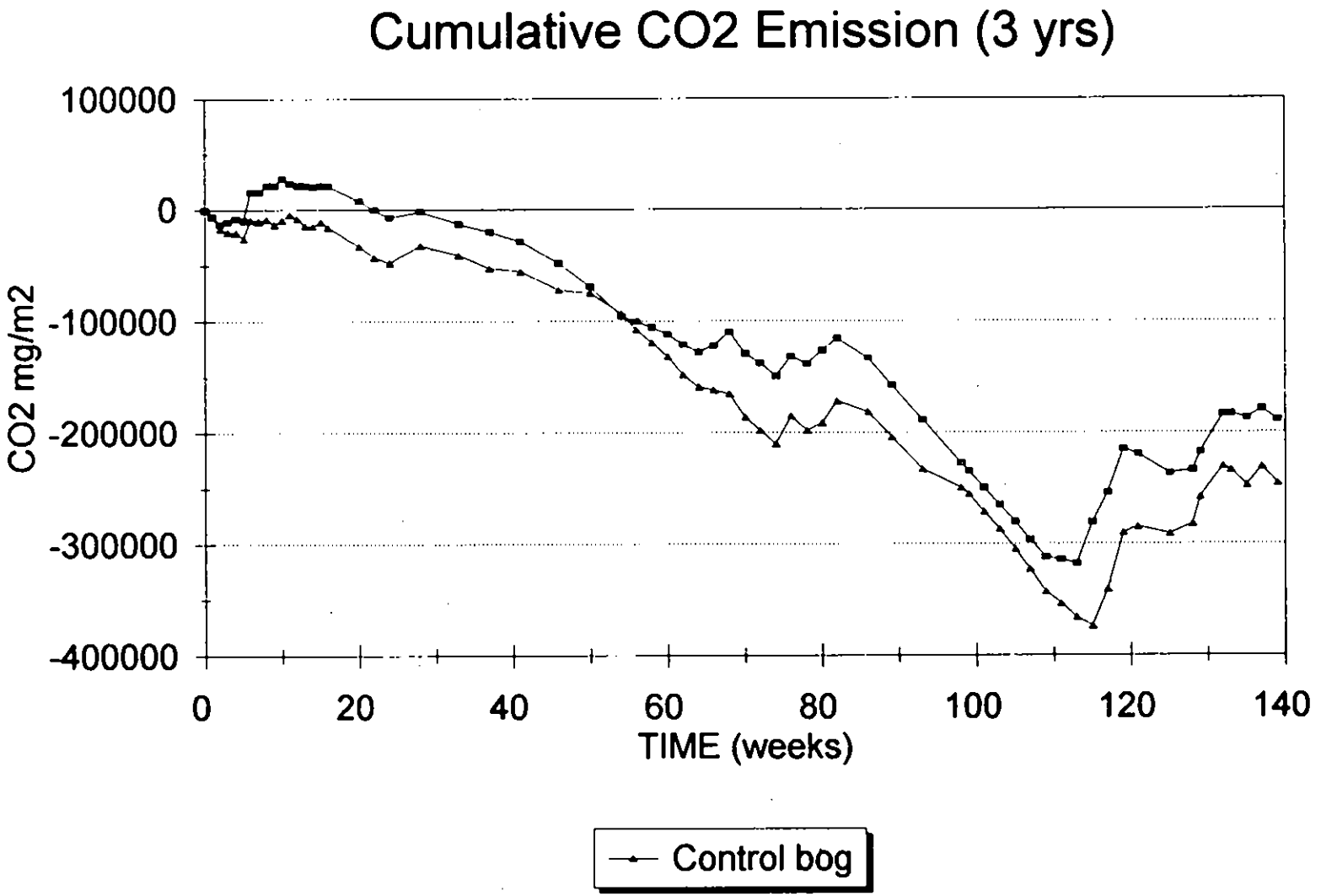
Cumulative CO2 Emission (3 yrs)
100000
0
-100000
-200000
-300000
-400000
CO2 mg/m2
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 6

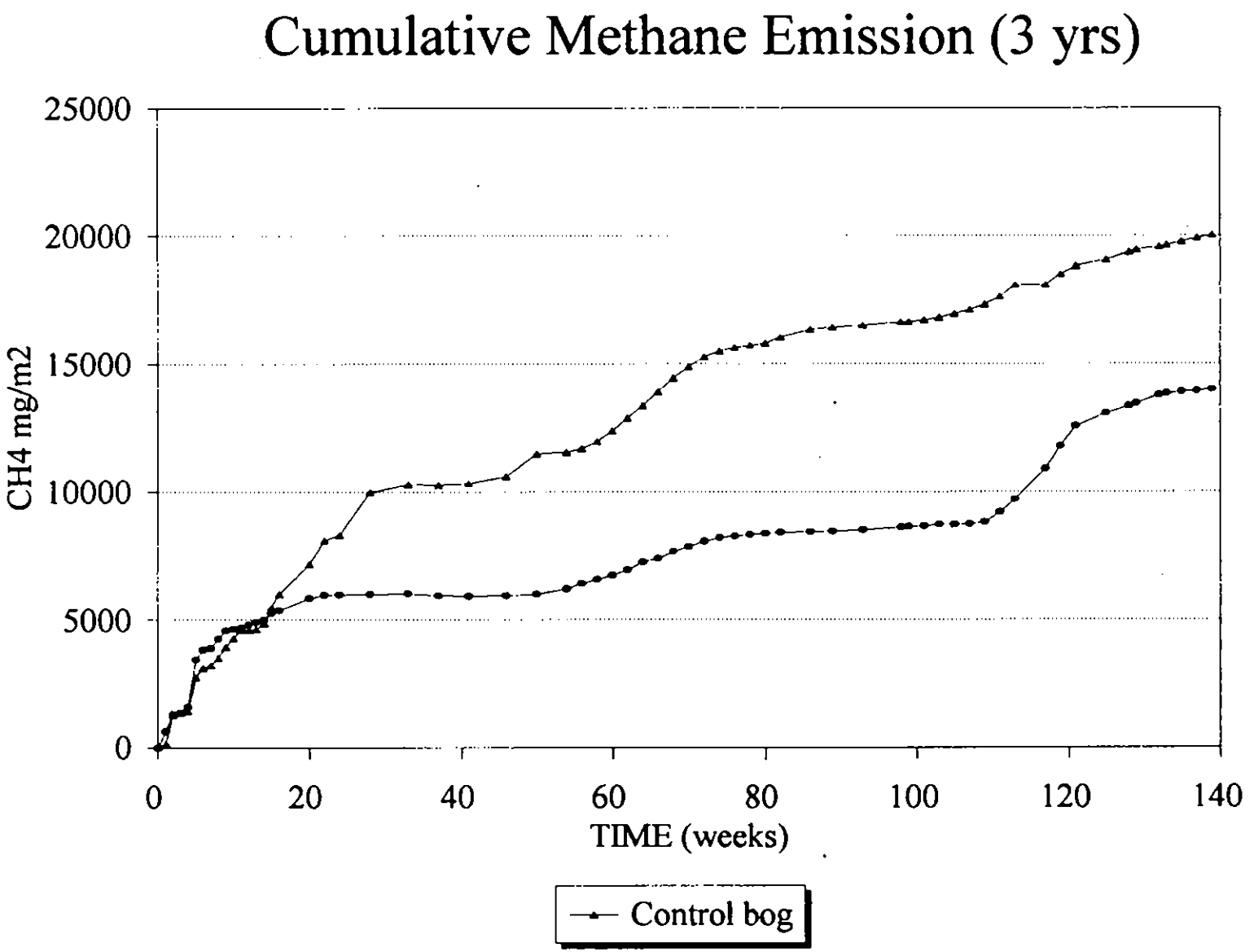
Cumulative Methane Emission (3 yrs)
25000
20000
15000
10000
5000
0
CH4 mg/m2
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 7

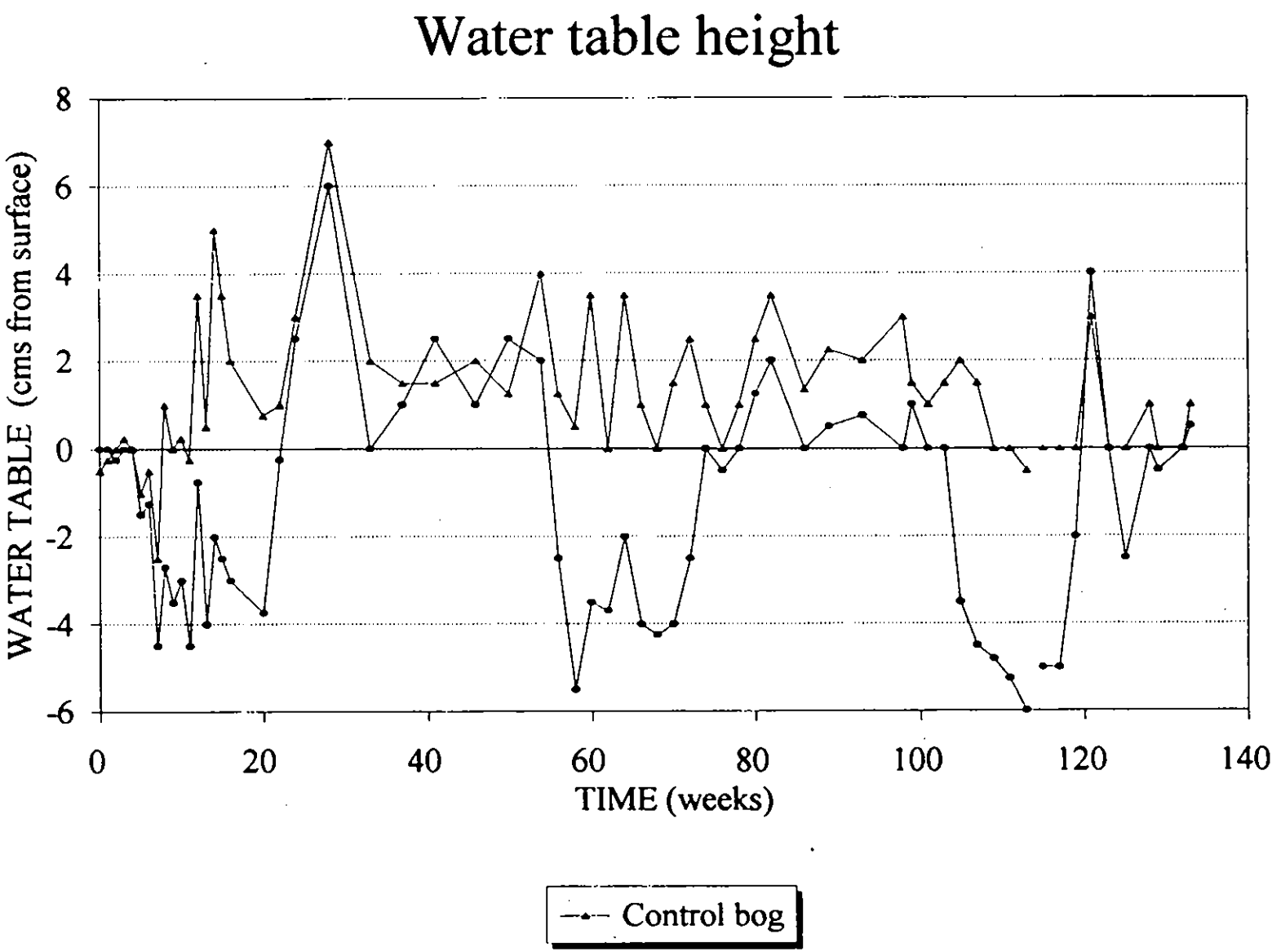
Water table height
WATER TABLE (cms from surface)
8
6
4
2
0
-2
-4
-6
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 8

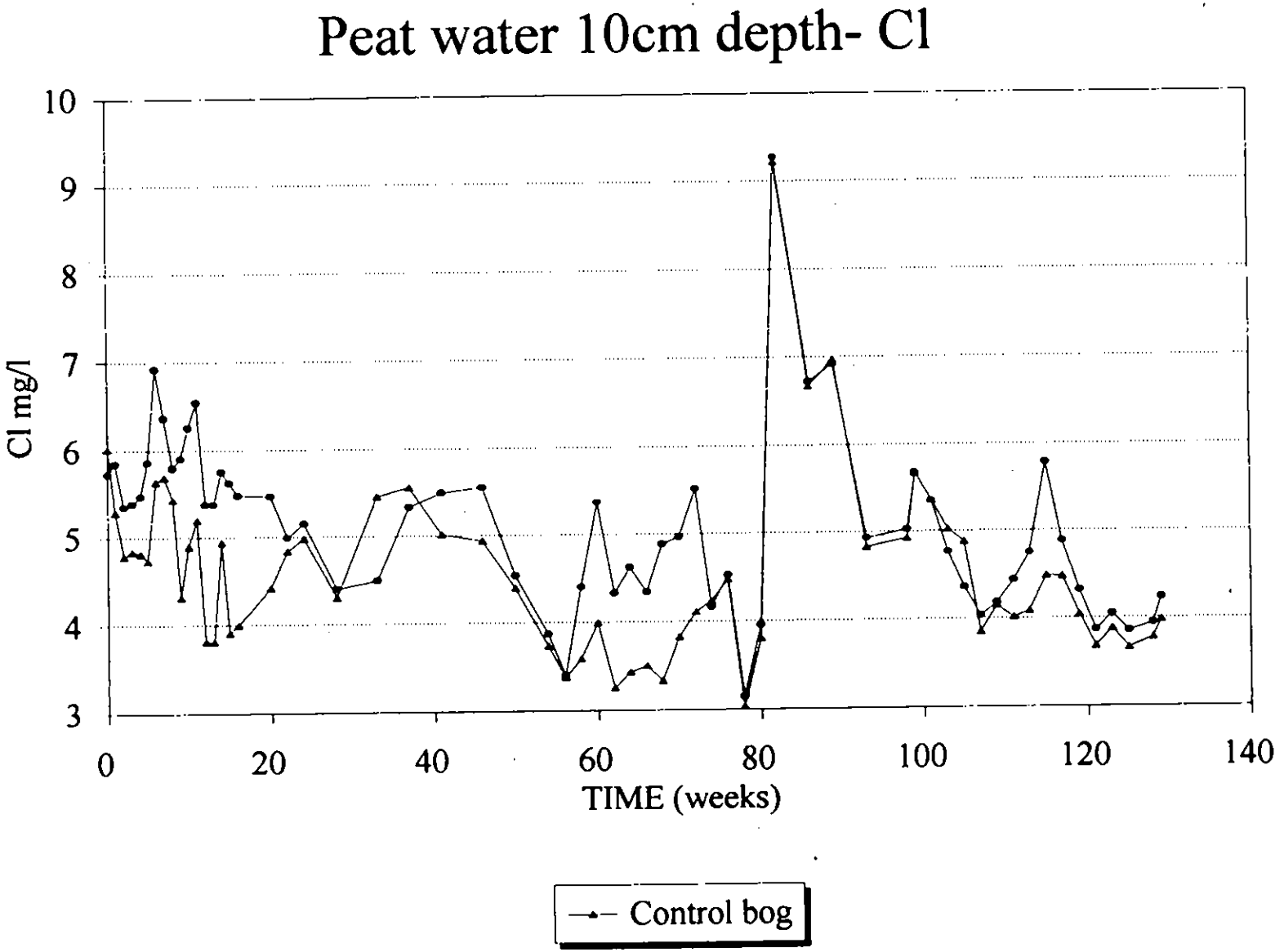
Peat water 10cm depth- Cl
Cl mg/l
10
9
8
7
6
5
4
3
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 9

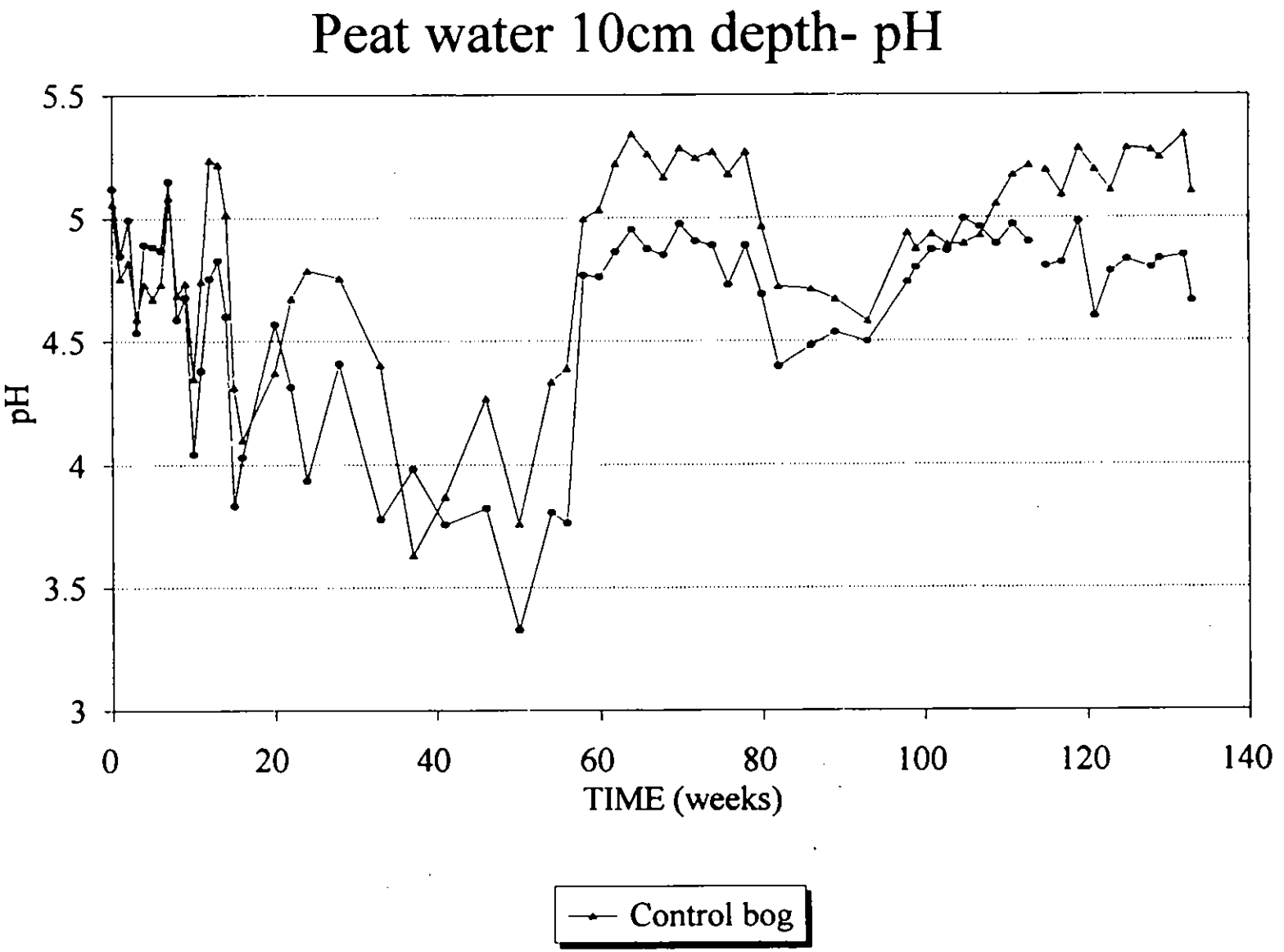
Peat water 10cm depth- pH
5.5
5
4.5
4
3.5
3
pH
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 10

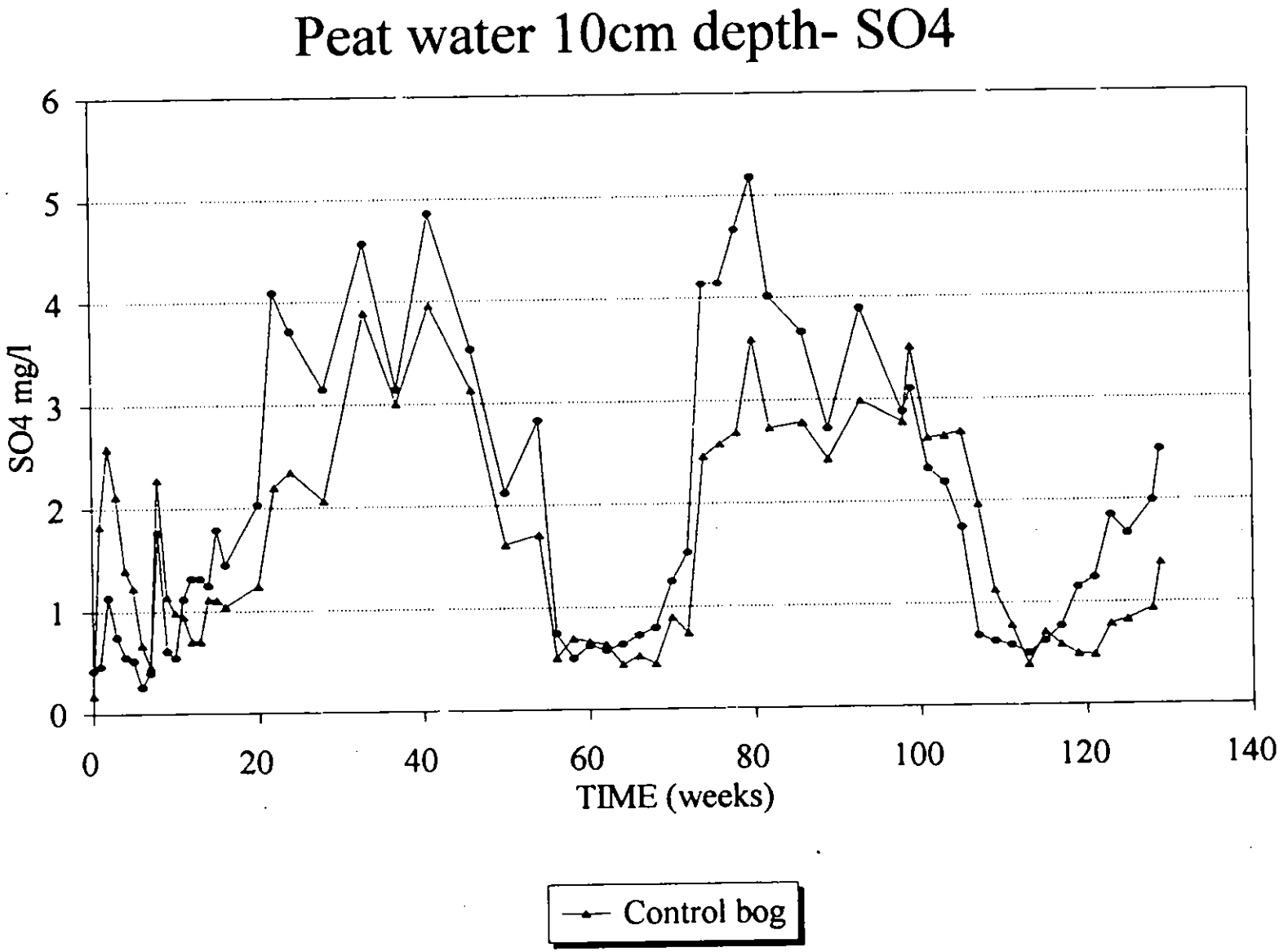
Peat water 10cm depth- SO4
SO4 mg/l
0
1
2
3
4
5
6
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 11

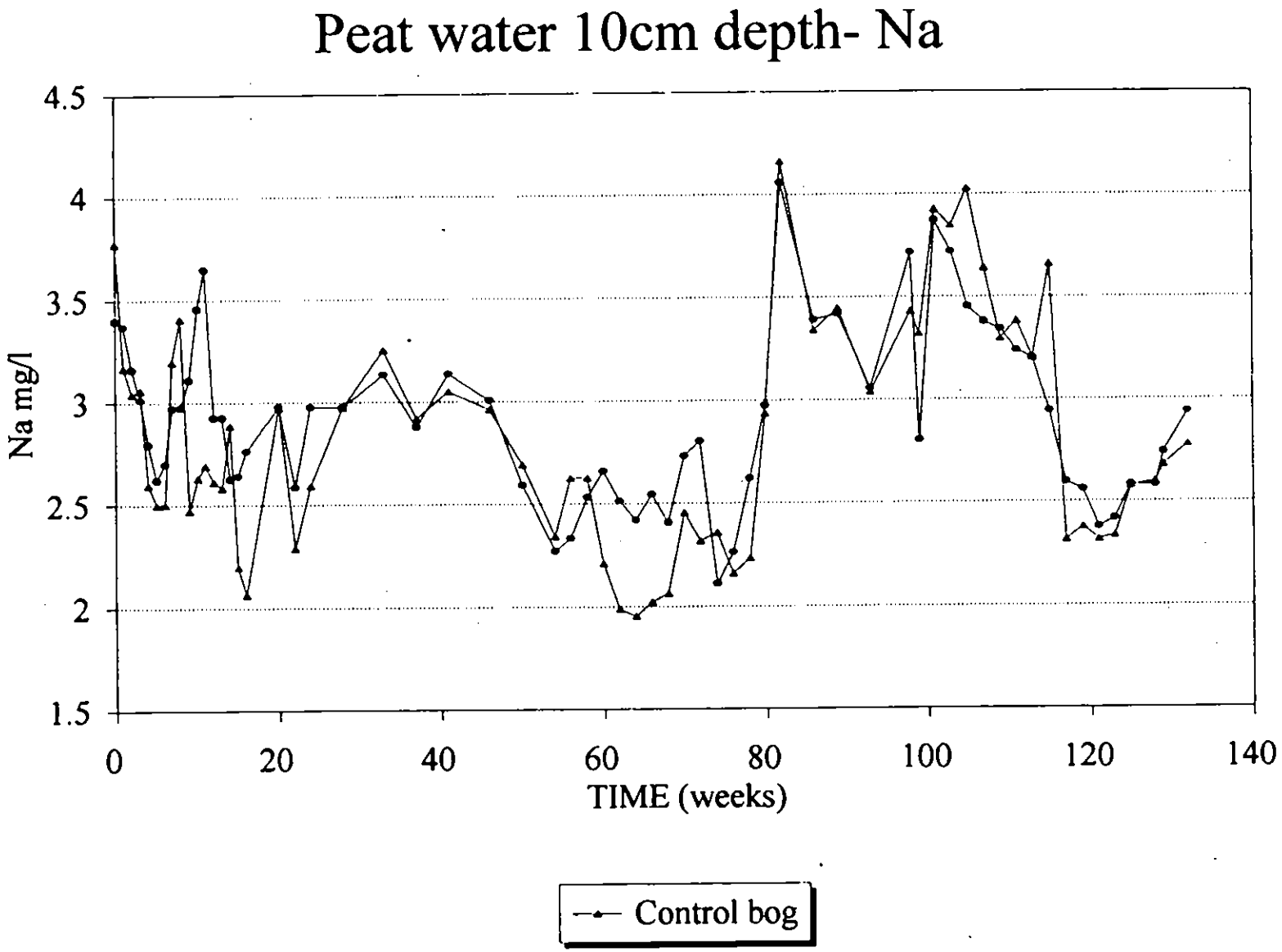
Peat water 10cm depth- Na
Na mg/l
4.5
4
3.5
3
2.5
2
1.5
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 12

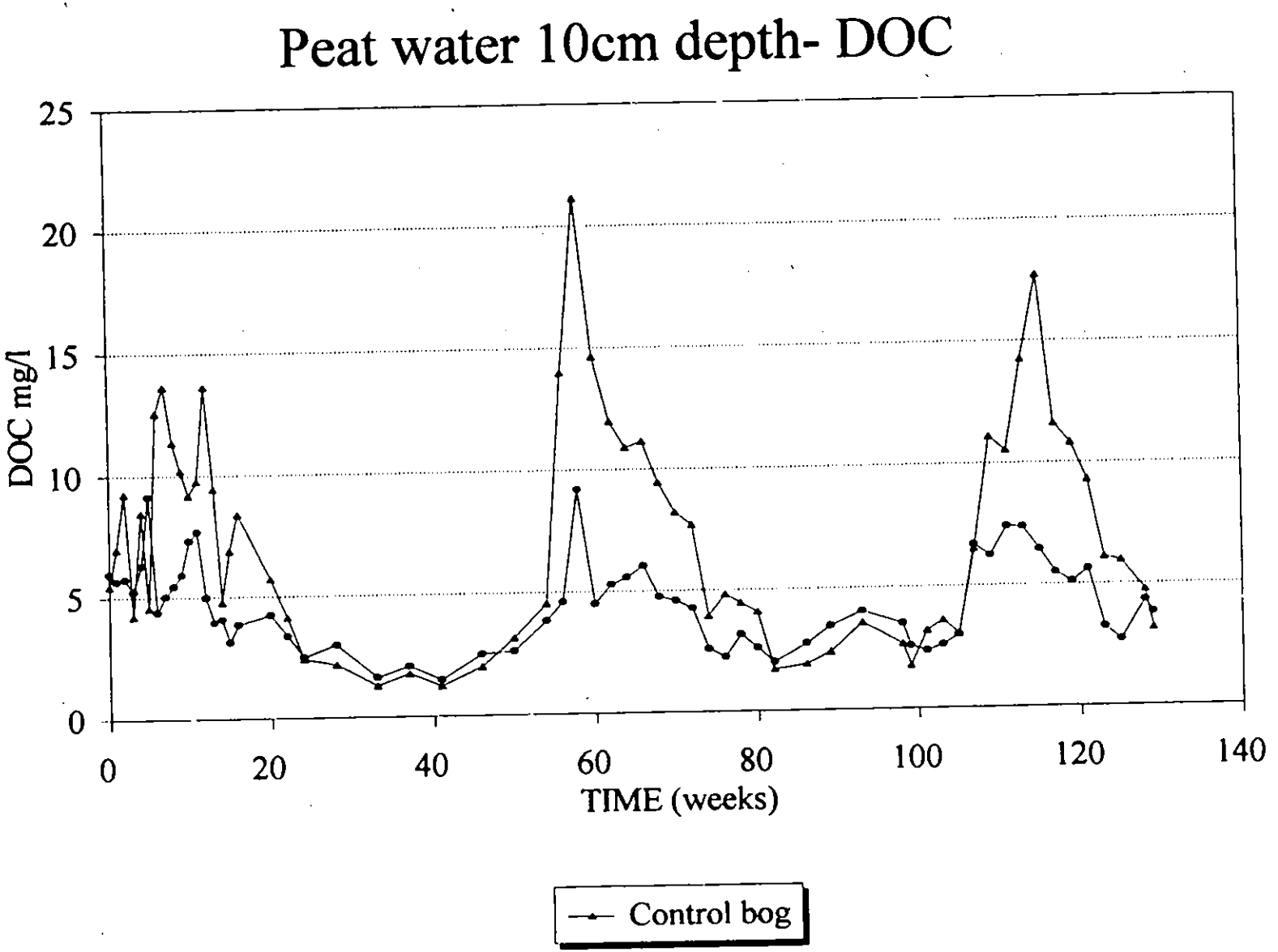
Peat water 10cm depth- DOC
DOC mg/l
25
20
15
10
5
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 13

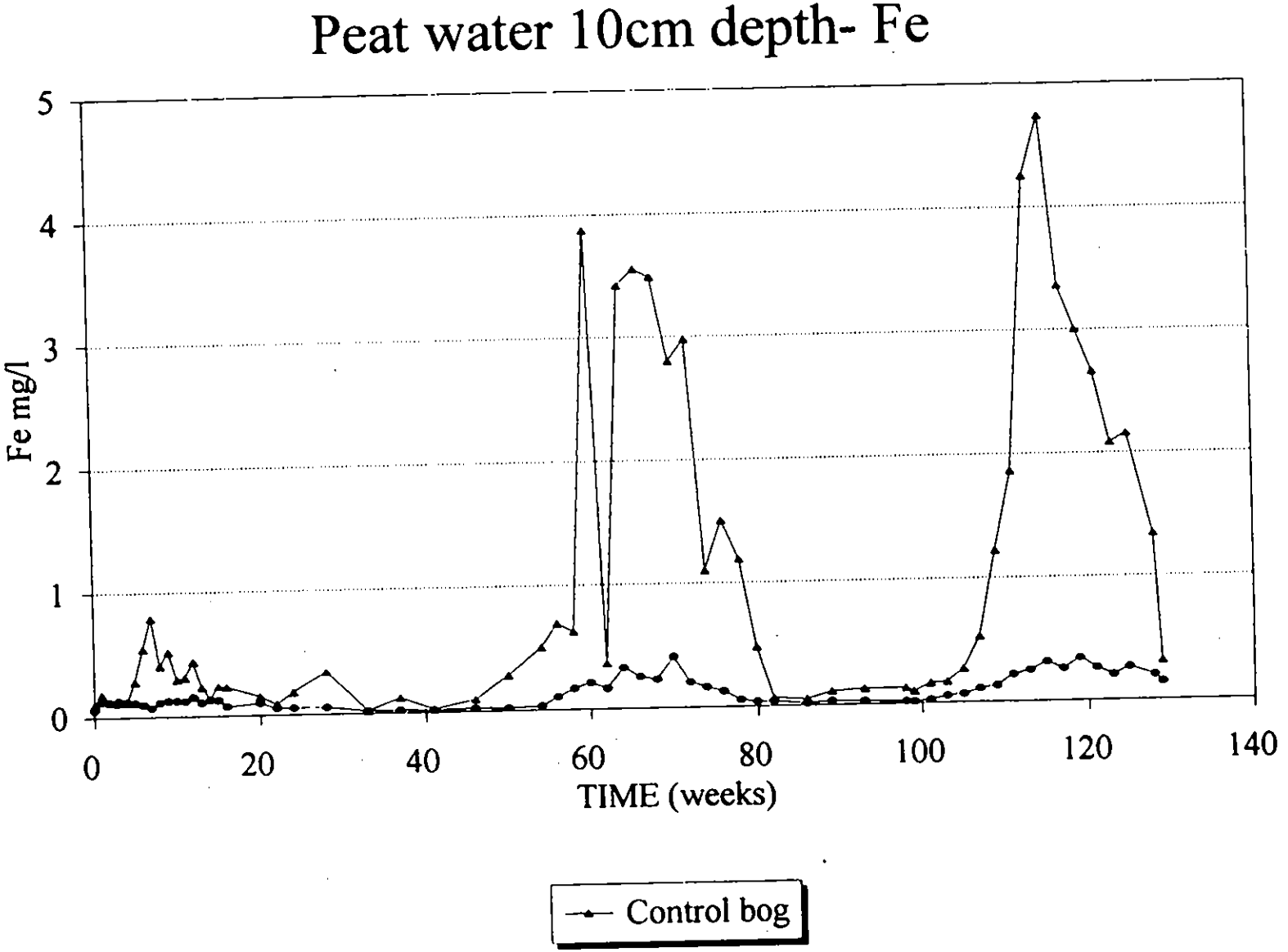
Peat water 10cm depth- Fe
Fe mg/l
0
1
2
3
4
5
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 14

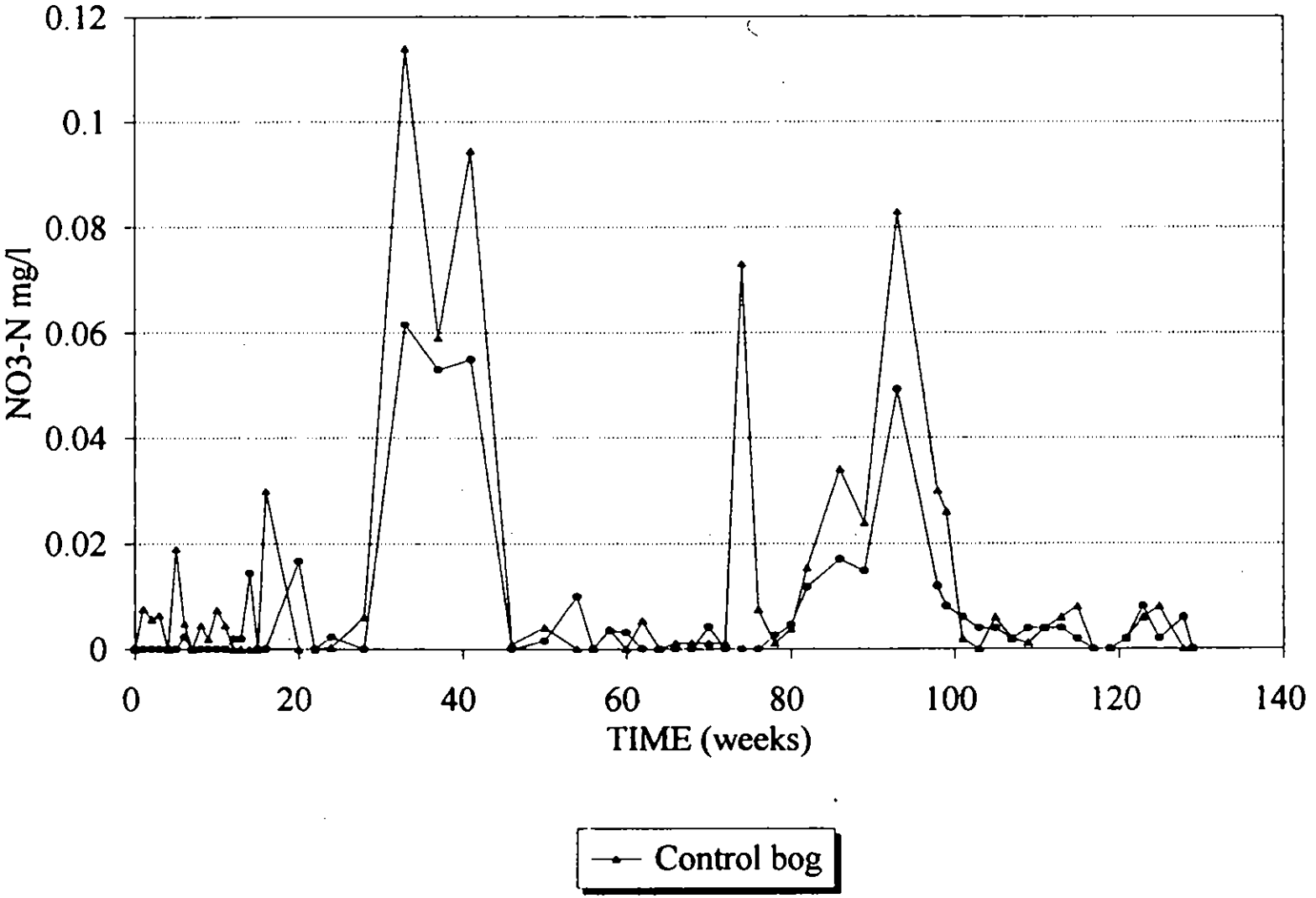
Peat water 10cm depth- NO3-N
0.12
0.1
0.08
0.06
0.04
0.02
0
NO3-N mg/l
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 15

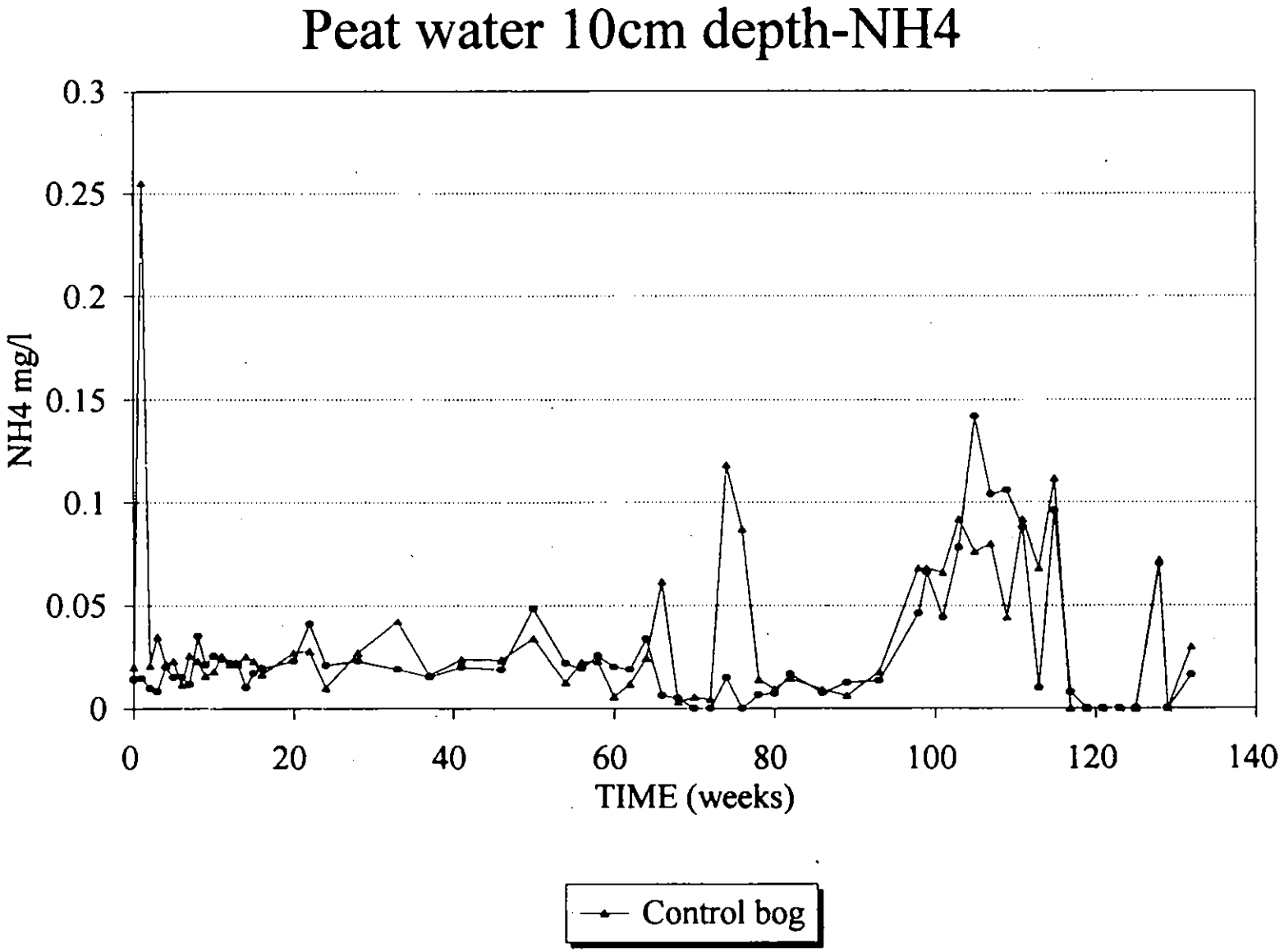
Peat water 10cm depth-NH4
NH4 mg/l
0.3
0.25
0.2
0.15
0.1
0.05
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 16

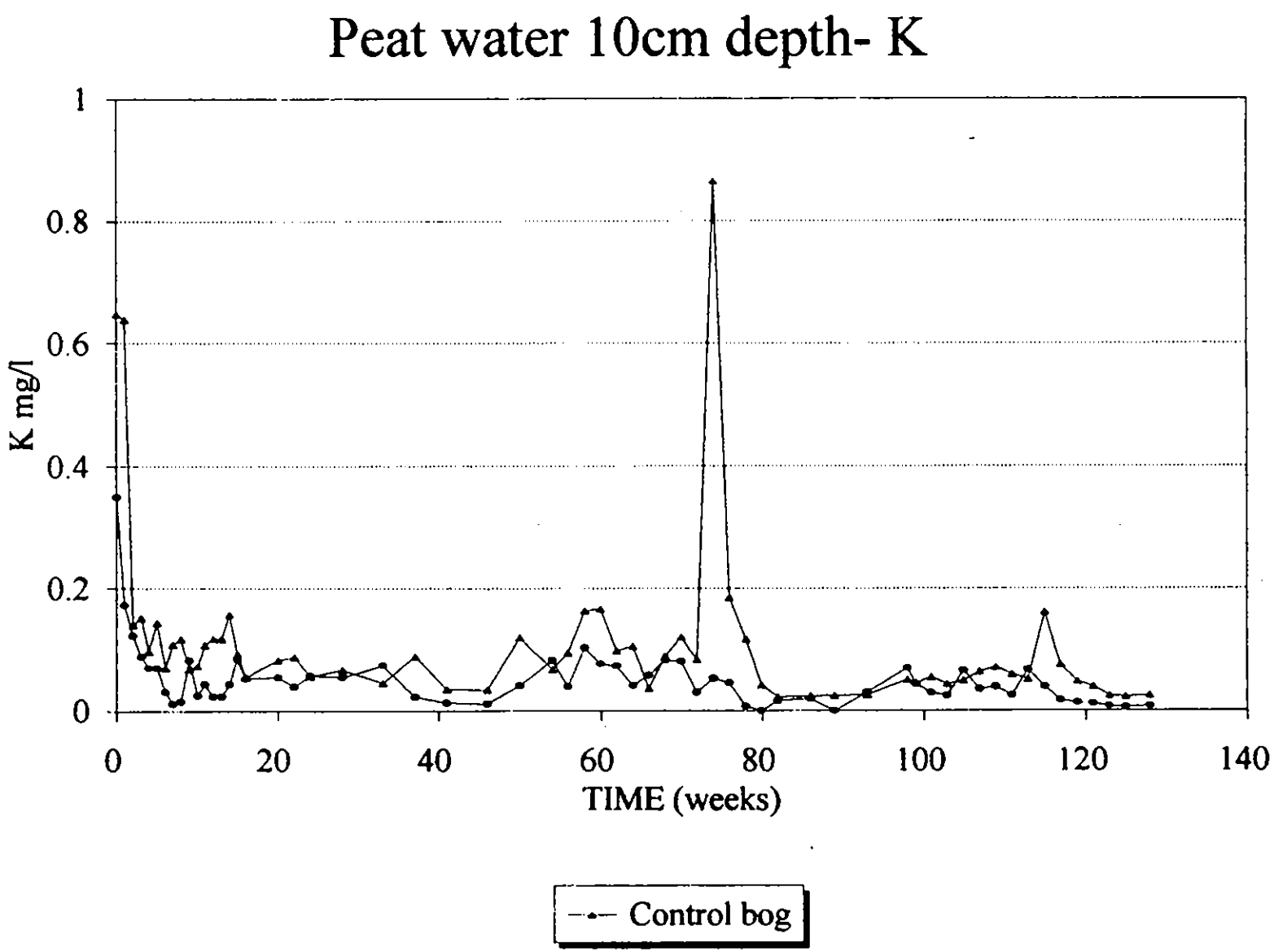
Peat water 10cm depth- K
K mg/l
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 17

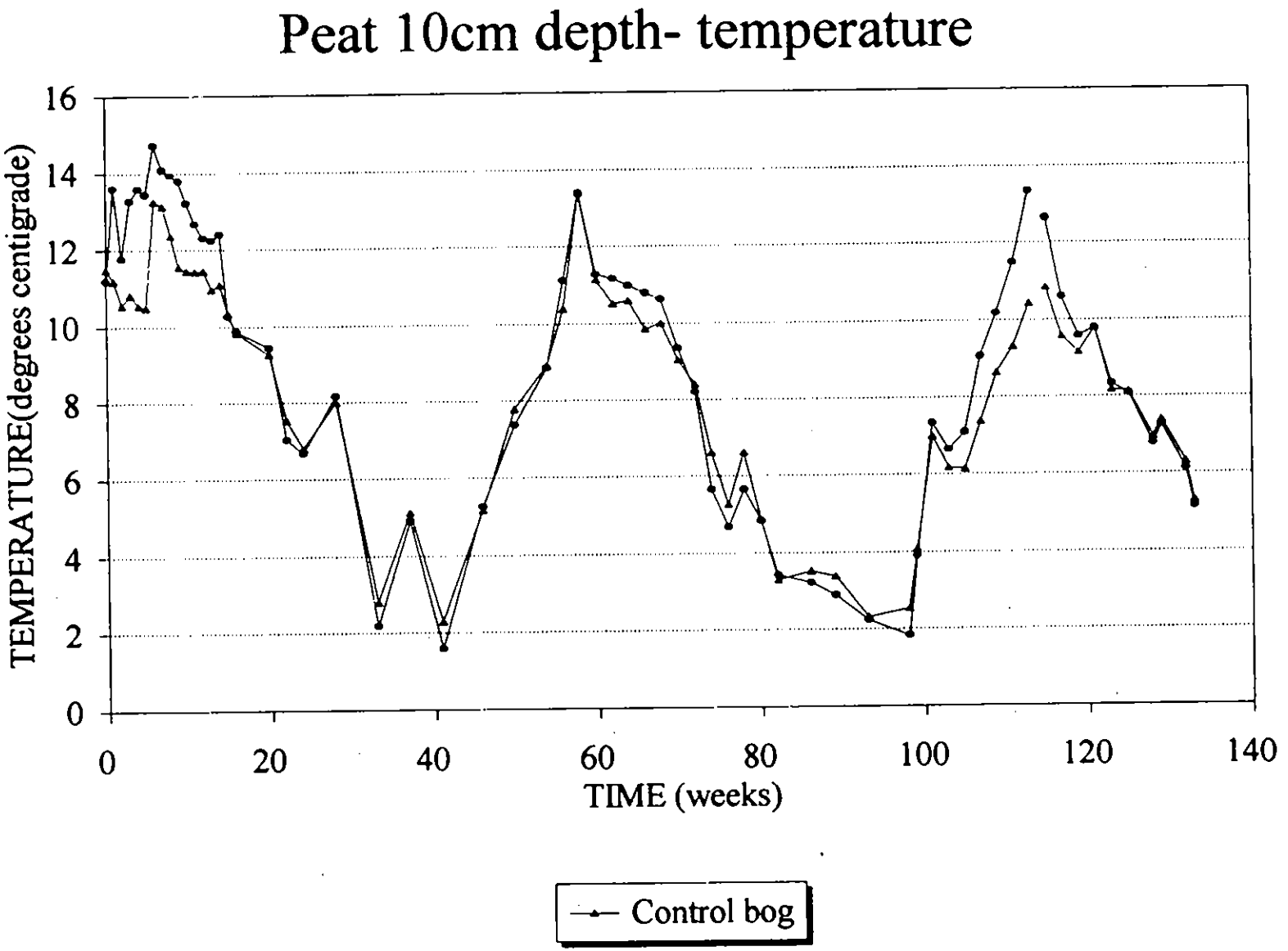
Peat 10cm depth- temperature
TEMPERATURE(degrees centigrade)
0
2
4
6
8
10
12
14
16
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 18

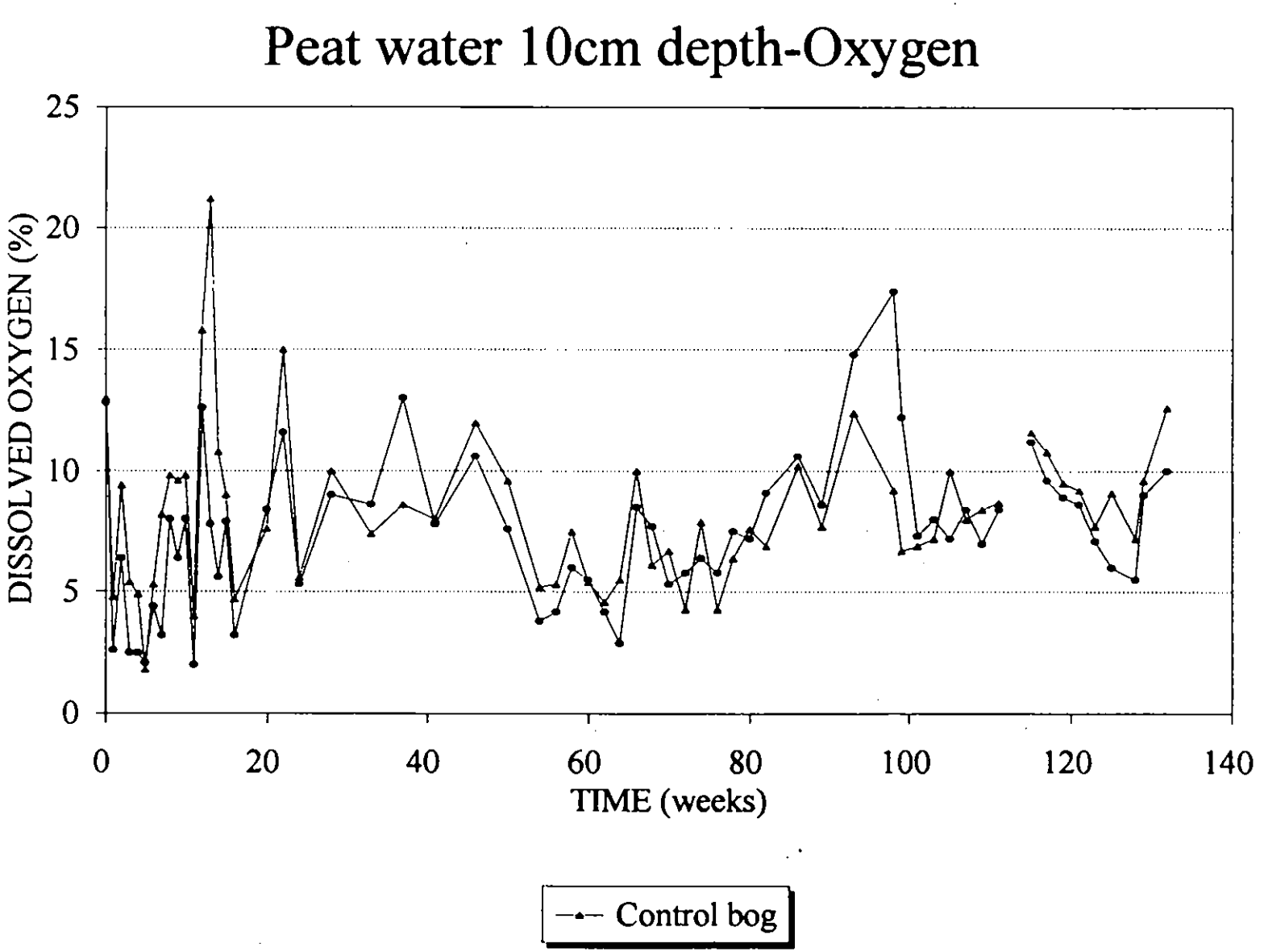
Peat water 10cm depth-Oxygen
DISSOLVED OXYGEN (%)
25
20
15
10
5
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 19

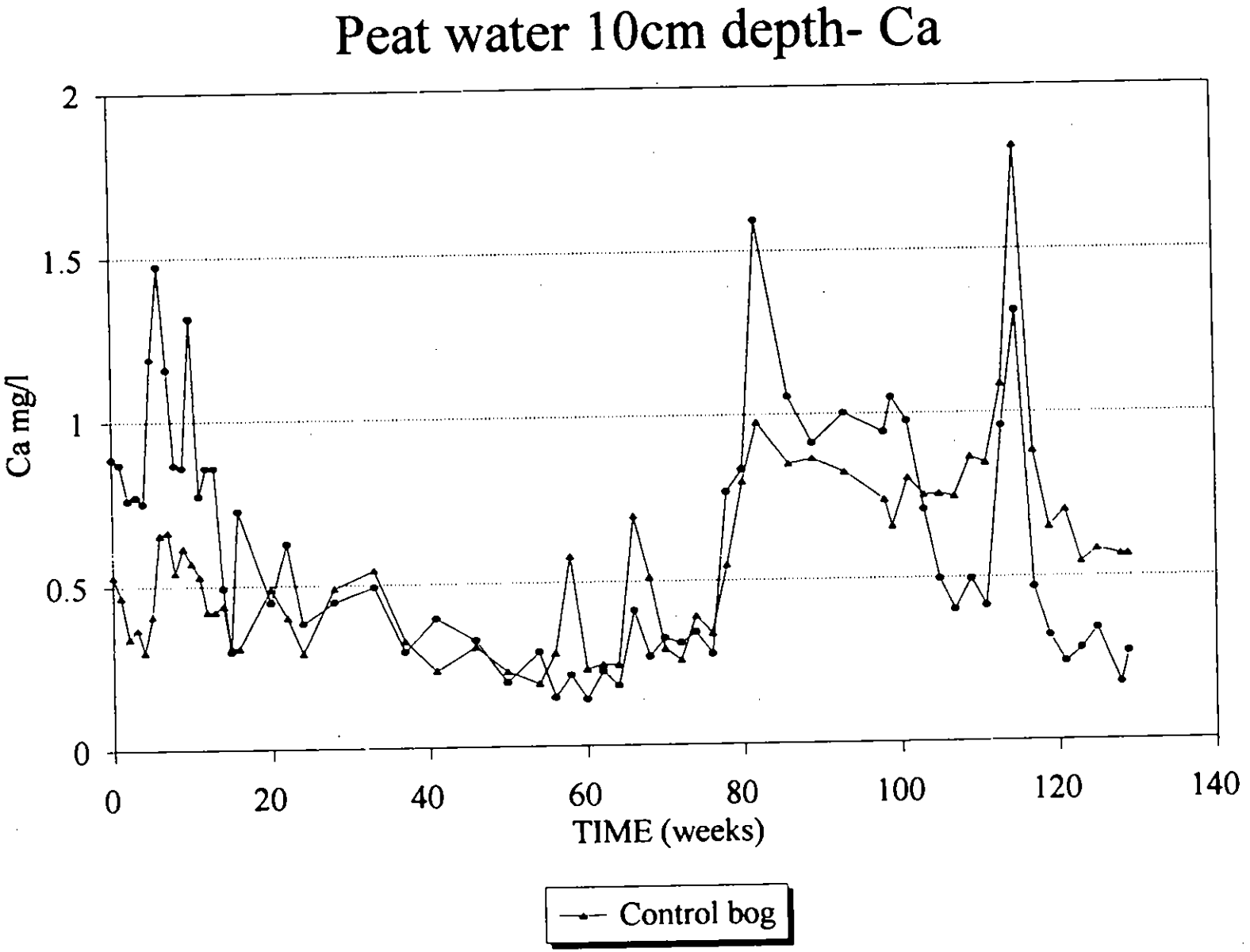
Peat water 10cm depth- Ca
Ca mg/l
2
1.5
1
0.5
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 20

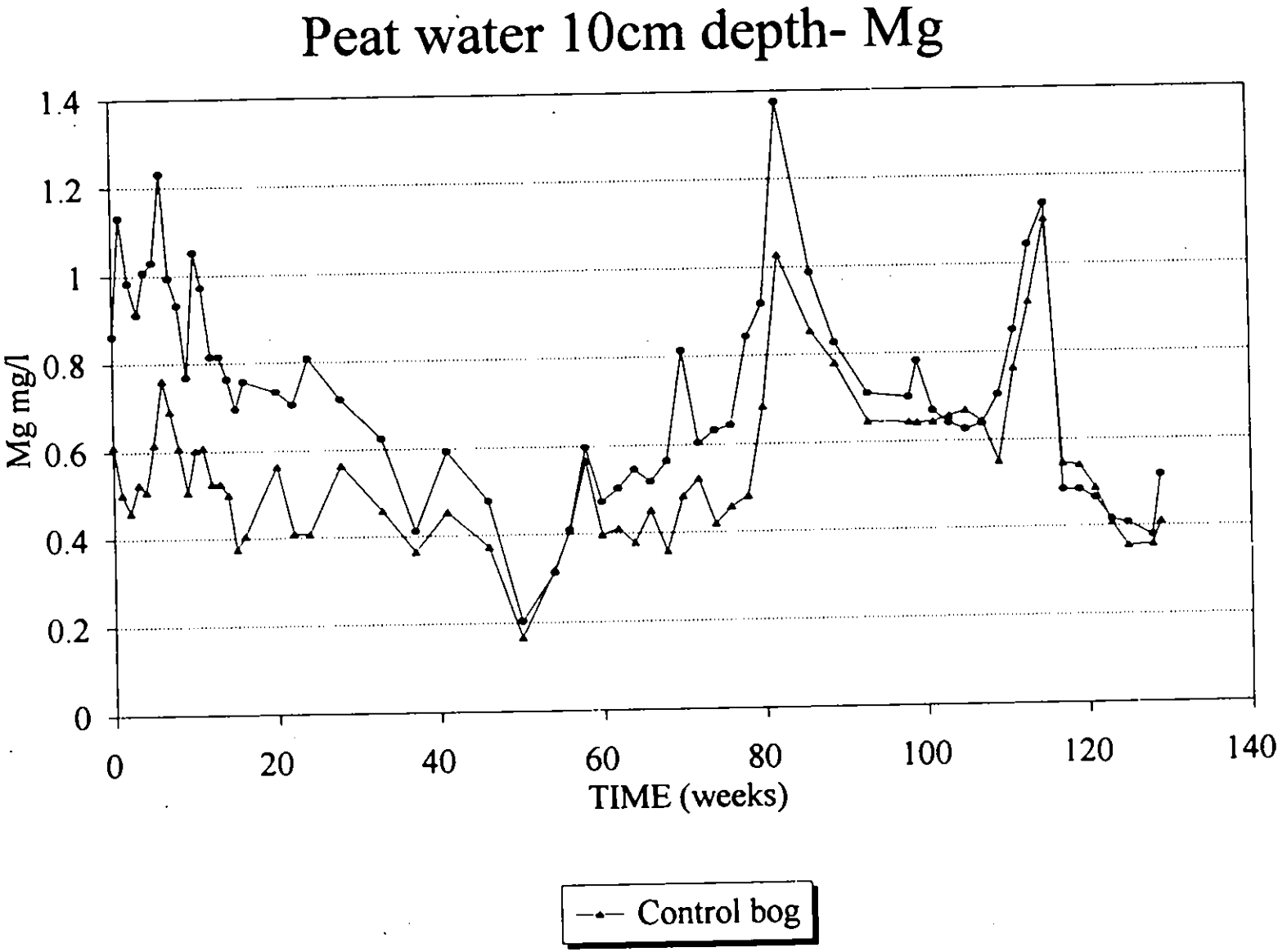
Peat water 10cm depth- Mg
Mg mg/l
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
120
140
TIME (weeks)
Control bog

Figure 21

Natural
Environment
Research
Council